Synthesis and Characterization of New Diiron and Diruthenium μ-Aminocarbyne Complexes Containing Terminal S-, P- and C-Ligands

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Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65th birthday

The diiron aminocarbyne complexes $[Fe_2\{\mu\text{-CN(Me)}(R)\}(\mu\text{-CO})(CO)(NCMe)(Cp)_2][SO_3CF_3]$ (R = Xyl, **1a**; R = Me, **1b**; R = CH_2Ph, **1c**; Xyl = 2,6-$Me_2C_6H_3$) undergo replacement of the coordinated nitrile by halides, diethyldithiocarbamate, and dicyanomethanide to give $[Fe_2\{\mu\text{-CN(Me)}(R)\}(\mu\text{-CO})(CO)(X)(Cp)_2]$ complexes (R = Me, X = Br, **4a**; R = Me, X = I, **4b**; R = CH_2Ph, X = Cl, **4c**; R = CH_2Ph, X = Br, **4d**; R = CH_2Ph, X = I, **4e**; R = Xyl, X = $SC(S)NEt_2$, **5a**; R = Me, X = $SC(S)NEt_2$, **5b**; R = Xyl, X = $CH(CN)_2$, **7**), in good yields. The molecular structure of **5a** shows an unusual η^1 coordination mode of the dithiocarbamate ligand. Similarly, treatment of $[M_2\{\mu\text{-CN(Me)}(R)\}(\mu\text{-CO})(CO)(NCMe)(Cp)_2][SO_3CF_3]$ (M = Fe, R = Xyl, **1a**; M = Fe, R = Me, **1b**; M = Ru, R = Xyl, **2a**; M = Ru, R = Me, **2b**) with a series of phosphanes generates the cationic complexes $[M_2\{\mu\text{-CN(Me)}(R)\}(\mu\text{-CO})(CO)(P)(Cp)_2][SO_3CF_3]$ (M = Fe, R = Xyl, P = PPh_2H, **6a**; M = Fe, R = Xyl, P = PPh_3, **6b**; M = Fe, R = Xyl, P = PMe_3, **6c**; M = Fe, R = Me, P = PMe_2Ph, **6d**; M = Fe, R = Me, P = PPh_3, **6e**; M = Fe, R = Me, P = $PMePh_2$, **6f**; M = Ru, R = Xyl, P = PPh_2H, **6g**; M = Ru, R = Me, P = PPh_2H, **6h**), in high yields. The molecular structure of **6a** has been elucidated by an X-ray diffraction study. The reactions of $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(NCR')(Cp)_2][SO_3CF_3]$ [R' = Me, **1a**; R' = tBu, **3**] with PhLi and PPh_2Li yield $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(Ph)(Cp)_2]$ (**8**) and $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(PPh_2)(Cp)_2]$ (**9**), respectively. The molecular structure of **8** has been ascertained by X-ray diffraction. Conversely, the reaction of **1a** with MeLi generates the aminoalkylidene compound $[Fe_2\{C(Me)N(Me)(Xyl)\}(\mu\text{-CO})_2(CO)(Cp)_2]$ (**10**).

Finally, the acetone complex $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(OCMe_2)(Cp)_2][SO_3CF_3]$ (**12**) reacts with lithium acetylides to give complexes $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(C{\equiv}CR)(Cp)_2]$ (R = p-C_6H_4Me, **11a**; R = Ph, **11b**; R = $SiMe_3$, **11c**), in high yields. Filtration through alumina of a solution of **11a** in CH_2Cl_2 results in hydration of the acetylide group and C–Si bond cleavage, affording $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)\{C(O)Me\}(Cp)_2]$ (**12**).

Key words: Diiron Complexes, Carbyne, Alkynyl, Nitrile Ligands, Crystal Structures

Introduction

Nitrile ligands are of widespread use in coordination and organometallic chemistry. They usually behave as labile ligands and their complexes are often considered equivalent to coordinatively unsaturated species. However, in a number of cases, metal coordination results in activation of nitriles toward nucleophilic addition. Examples include the additions of amines, alcohols and water, which have provided routes to transform nitriles into the corresponding azavinylidenes, amides, imidic esters, and aminidines [1].

We have found that nitrile ligands in dinuclear complexes of the type $[M_2\{\mu\text{-CN(Me)}(R)\}(\mu\text{-CO})(CO)(NCMe)(Cp)_2][SO_3CF_3]$ [M = Fe, R = Xyl, **1a**; M = Fe, R = Me, **1b**; M = Fe, R = CH_2Ph, **1c**; M = Ru, R = Xyl, **2a**; M = Ru, R = Me, **2b**] and $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(NC{t}Bu)(Cp)_2][SO_3CF_3]$ (**3**) can react in both ways. Thus, nitriles in **1** – **3** are easily displaced by a number of different ligands, including hydride, cyanide and halides [2], thiocyanide and azide [3], amines and imines [4]. Displacement of nitrile ligands by phosphanes has been described for the analogous aminocarbyne complexes $[Fe_2\{\mu\text{-CN(Me)}_2\}_2(CO)(NCR)(Cp)_2][SO_3CF_3]_2$ [5].

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Moreover, MeCN displacement by alkynes is assumed to occur as a preliminary step in the observed alkyne insertion into the metal-carbyne bond of complexes **1** and **2** [6].

On the other hand, examples of nucleophilic addition involving the nitriles in **1** – **3** are also known. In particular, the addition of acetylides to the nitrile ligand in complexes $[M_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(\text{CO})(\text{NC}t\text{Bu})(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ (M = Fe, Ru) results in the formation of azavinylidene intermediates, which can be transformed into the alkynyl-imine complexes $[M_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(\text{CO})\{\text{N(H)} = \text{C}(t\text{Bu})(\text{C}{\equiv}\text{CR}')\}(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ [7]. Likewise, arylnitrile ligands in $[\text{Fe}_2\{\mu\text{-CN(Me)}(R)\}(\mu\text{-CO})(\text{CO})(p\text{-NCC}_6\text{H}_4\text{R}')(\text{Cp})_2]^+$ have been shown to undergo nucleophilic addition of acetylides [8].

Herein, we report an extension of the nitrile substitution reactions on complexes **1** – **3**, including different S-, P- and C-ligands.

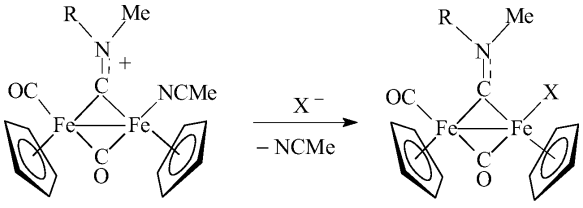
Results and Discussion

Substitution reactions in diiron and diruthenium aminocarbyne complexes

We have previously reported on the substitution of the MeCN ligand in **1a** by halides, to afford the complexes $[\text{Fe}_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(\text{CO})(X)(\text{Cp})_2]$ [X = Cl, Br, I] [2]. Now we have found that the aminocarbyne complexes **1b** and **1c** also react with an excess of LiCl, LiBr, or KI in refluxing CH_2Cl_2 to form the corresponding halide complexes **4a** – **e** in good yields (Scheme 1). The substitution reaction can be extended to other ligands. Thus, **1a** and **1b** react with $NaSC(S)NEt_2$ resulting in the formation of the dithiocarbamate complexes **5a** and **5b**, respectively (Scheme 1).

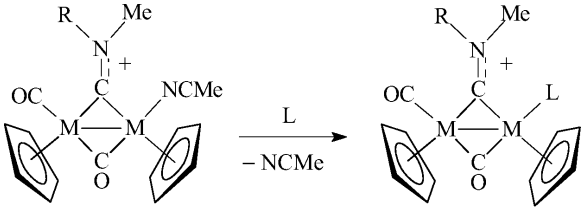
Likewise, phosphanes can replace the acetonitrile ligand in compounds **1** and **2**. Hence, the complexes **6a** – **h** have been obtained in high yield by treatment of the diiron complexes **1a** – **b** and diruthenium complexes **2a** – **b** with a variety of phosphanes (Scheme 2).

All compounds **4** – **6** were purified by chromatography on alumina and characterized by IR and NMR spectroscopy and elemental analysis. The molecular structures of **5a** and **6a** have been ascertained by X-ray diffraction studies (see below). The IR spectra (in CH_2Cl_2 solution) of **4** – **6** exhibit the usual pattern consisting of terminal and bridging carbonyl absorptions. The ^{1}H NMR spectra of **4c** – **e**, **5a**, **6a** – **c**, **6g**, reveal



	R	X	
1b	Me	Br	**4a**
1b	Me	I	**4b**
1c	CH_2Ph	Cl	**4c**
1c	CH_2Ph	Br	**4d**
1c	CH_2Ph	I	**4e**
1a	Xyl	$SC(S)NEt_2$	**5a**
1b	Me	$SC(S)NEt_2$	**5b**

Scheme 1.



	M	R	L	
1a	Fe	Xyl	PPh_2H	**6a**
1a	Fe	Xyl	PPh_3	**6b**
1a	Fe	Xyl	PMe_3	**6c**
1b	Fe	Me	PMe_2Ph	**6d**
1b	Fe	Me	PPh_3	**6e**
1b	Fe	Me	$PMePh_2$	**6f**
2a	Ru	Xyl	PPh_2H	**6g**
2b	Ru	Me	PPh_2H	**6h**

Scheme 2.

the presence of two isomers. These are attributable to the different orientations that R (CH_2Ph or Xyl) and Me can assume with respect to the non-equivalent Fe or Ru atoms as a consequence of the double bond character of the μ-C-N interaction. As usually found in this type of complexes, the isomers are present in comparable amounts when R = CH_2Ph, whereas the E isomer prevails for R = Xyl [2 – 4]. This behaviour is simply explained on the ground of steric arguments, since the more favourable configuration has the sterically demanding groups N-Xyl and L pointing in opposite directions (see Chart 1).

Due to the mutual Cp position (*cis* and *trans* isomers) further isomeric forms are, in theory, possible. However, IR and NMR data, including NOE investigations, indicate that compounds **4** – **6**, in solution, are exclusively *cis*. This is consistent with the fact that analogous complexes containing the

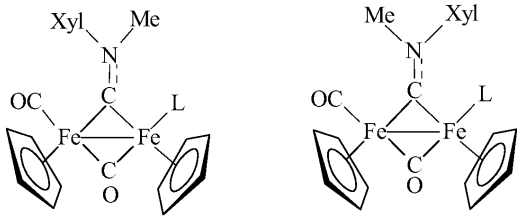
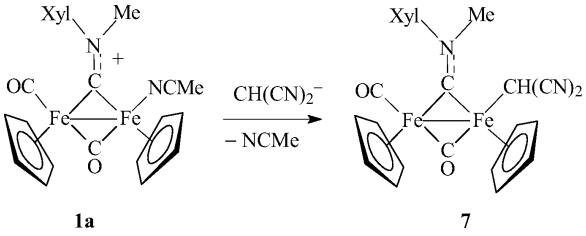


Chart 1. *E*-*Z* isomers in diiron μ-aminocarbyne complexes.



Scheme 3.

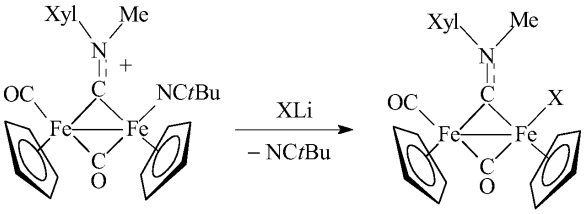
$[Fe_2(CO)_2Cp_2]$ frame are predominantly *cis*. Examples of the less common *trans* isomers include the related compound $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(NCS)(Cp)_2]$ [3]. This complex was obtained from **1a** by replacing MeCN with SCN^- at r. t., and quantitatively converted into the corresponding *cis* isomer upon heating at reflux in THF, suggesting that nitrile substitutions might proceed *via* the formation of *trans* intermediates which, then, isomerize to the more stable *cis* form. In the light of these considerations, we have performed some of the reactions described in Schemes 2 and 3 at r. t., with the aim of isolating, or merely observing, the *trans* isomers of the described products. Only in one case, namely in the reaction of **1b** with KBr, we were able to obtain **4a** as a *cis*-*trans* isomeric mixture (see details in the experimental part). As expected, the reactions are sluggish and conversions are slower when performed at r. t.

Complexes **5a**–**b** contain a dithiocarbamate ligand in an unusual η^1-coordination mode (see below). Dithiocarbamate ligands are usually coordinated in an η^2-fashion, both in poly- [9] and in mononuclear species [10]. The η^1-mode is less common, and is mainly found in mononuclear compounds [11], whereas only few cases have been reported for polynuclear complexes [12, 13]. To the best of our knowledge, **5a** represents the first example of a diiron compound containing an η^1-coordinated dithiocarbamate ligand. A medium-intensity band at 1458 cm^{-1}, observed in the IR spectrum (in KBr pellets) of **5a**, and assigned to the C–N interaction of the dithiocarbamate frame, confirms that the ligand is monodentate. The SCS carbon atom resonates at *ca.* 207 ppm.

It has to be remarked that the nitrile displacement described above provides an efficient route to the coordination of a variety of ligands, with higher yields and under milder reaction conditions than those of the corresponding CO displacements. Indeed, the carbonyl complexes $[Fe_2\{\mu\text{-CN(Me)(R)}\}(\mu\text{-CO})(CO)_2(Cp)_2][SO_3CF_3]$ undergo CO displacement only under irradiation or require higher thermal activation [5b]. On the other hand, it has to be noticed that not all the ligands replace MeCN so efficiently as those reported in Schemes 1 and 2. Thus, the reactions of **1a** with thiolates (*i. e.* PhSNa, *n*BuSNa) result in the formation of mixtures of decomposition products. Likewise, no reaction was observed between **1a**–**c** or **3** and ROH (R = Me, Et), unless performed in the presence of a base (*e. g.* Na_2CO_3). By this procedure, the known bridging hydride complex $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-H})(CO)_2(Cp)_2]$ [2a] was obtained from **1a** in about 50 % yield, together with minor amounts of other unidentified products.

Substitution of nitrile by a carbanionic reagent (*e. g.* LiR) should provide a direct route to the formation of Fe–C bonds, and the coordination of alkyls, aryls or alkynyl ligands. However, it has to be considered that diiron and diruthenium aminocarbyne complexes can react with LiR in a variety of ways. In fact, beside ligand substitution, other reaction paths are available: i) nucleophilic addition at CO or Cp ligands to give stable acyl and cyclopentadiene derivatives, respectively [14]; ii) reduction and fragmentation of the dinuclear frame [15]; iii) nucleophilic addition at the coordinated nitrile [7–8]; iv) removal of acidic protons [16]. This latter possibility was observed previously upon treatment of **1a**–**c** with LiR: the MeCN ligand is deprotonated and rearranges to a cyanomethyl group affording the complexes $[Fe_2\{\mu\text{-CN(Me)}(R)\}(\mu\text{-CO})(CO)(CH_2CN)(Cp)_2]$ [16a]. Therefore, replacement of nitriles by carbanionic ligands in **1**–**2** has been limited, so far, to the reaction with cyanide [2]. Other stabilized carbanions are possible candidates to replace nitriles in **1**–**2**, due to their lower basicity and nucleophilic character compared to LiR. Therefore, we first investigated the reaction between **1a** and $CH(CN)_2Na$. The reaction results in the formation of $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)\{CH(CN)_2\}(Cp)_2]$ (**7**) (Scheme 3).

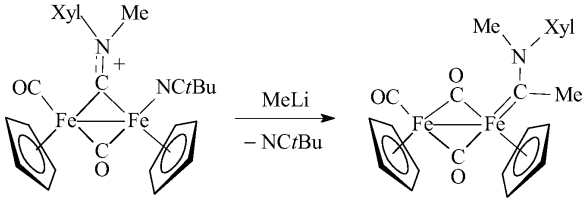
The spectroscopic features of **7** are consistent with those of the known cyanomethyl complex $[Fe_2\{\mu$-



3

X	
Ph	**8**
PPh_2	**9**

Scheme 4.



3 **10**

Scheme 5.

$CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(CH_2CN)(Cp)_2]$ [16a]. In particular, the IR spectrum of **7** exhibits a band assigned to the C≡N groups (at 2214 cm^{-1}), and the ^{13}C NMR resonance for $CH(CN)_2$ appers at low frequencies (−22.0 ppm). It has to be remarked that the reaction is not a general one and other stabilized carbanions, like β-diketonates, failed to produce the expected ligand substitution.

In order to favour the coordination of more basic ligands, avoiding deprotonation of the coordinated nitrile, we have investigated the trimethylacetonitrile complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(NCtBu)(Cp)_2][SO_3CF_3]$ (**3**) which does not contain acidic α-protons. Indeed, addition of LiPh to a THF solution of **3**, at −30 °C, produces the expected replacement of NC*t*Bu, yielding the σ-phenyl complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Ph)(Cp)_2]$ (**8**). Analogously, the complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(PPh_2)(Cp)_2]$ (**9**) was obtained by treatment of **3** with $LiPPh_2$ (Scheme 4). Compounds **8**–**9** have been characterized by spectroscopy and elemental analysis. The structure of **8** has been ascertained by X-ray diffraction studies and mass spectrometry.

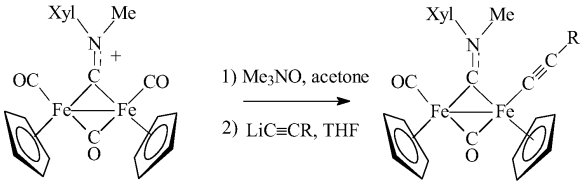
The NMR data of compound **8** definitely indicate the presence in solution of one isomeric form (*E* isomer), whereas significant amounts of the *Z* isomer are present in **9**. The low-frequency IR band of the bridging carbonyl in **8** (1775 cm^{-1}) accounts for the strong σ donation of the phenyl ligand. Several examples of mono- [17] and polynuclear [18] complexes of iron and ruthenium, containing phenyl groups acting as terminal η^1 ligands, have been reported. By contrast, only few cases of η^1-aryl-bridged complexes are known [19].

Interestingly, complex **9** can be obtained also by treatment of $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ with $LiPPh_2$, whereas attempts to generate **9** by deprotonation of the corresponding cationic species **6a** were unsuccessful.

Unlike LiPh, LiMe fails to produce, upon reaction with **3**, the expected σ-methyl complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Me)(Cp)_2]$. The reaction affords the terminally bonded aminoalkylidene compound $[Fe_2\{C(Me)N(Me)(Xyl)\}(\mu\text{-}CO)_2(CO)(Cp)_2]$ (**10**) (Scheme 5), which was isolated in low yield, among other unidentified decomposition products.

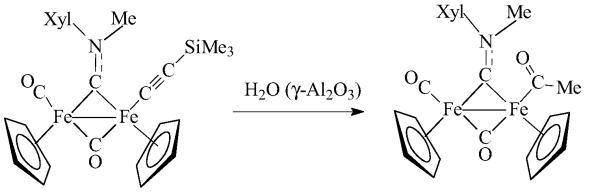
Complex **10** has been characterized by spectroscopy and elemental analysis. Its spectroscopic features are remarkably similar to those of related diiron aminoalkylidene complexes of the type $[Fe_2\{CHN(Me)(R)\}(\mu\text{-}CO)_2(CO)(Cp)_2]$ [*R* = Me, Et], previously reported [20]. The IR band pattern, in the carbonyl region, consists of two strong absorptions at 1932 and 1710 cm^{-1}, which accounts for one terminal and two bridging CO ligands. The aminocarbene carbon resonance at δ = 275.5 ppm is within the typical range of aminoalkylidene signals. The formation of **10** is presumably the result of a nucleophilic attack of CH_3^- at the bridging carbyne carbon atom of **3**. Generation of the aminocarbene ligand is followed by a shift of the ligand from the bridging to the terminal position, in agreement with the ascertained higher stability of the terminal coordination [20]. However, other mechanisms should not be excluded. In fact, the reaction might proceed *via* displacement of the nitrile, followed by intramolecular coupling between the methyl and the aminocarbyne ligands. In both cases, an additional CO ligand, probably arising from some parallel decomposition reactions, is required to provide stabilization to the otherwise unsaturated species. Finally, it is worth noting that the corresponding reaction of $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ with LiMe was reported to proceed *via* selective nucleophilic attack at the Cp ligand, affording the complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)_2(Cp)(C_5H_5Me)]$ [14]. Therefore, the presence of a nitrile ligand in the place of a carbonyl group completely changes the reaction outcome.

The reactions of **1**–**3** with acetylides are known to proceed *via* deprotonation of MeCN or nucle-



R	
p-C_6H_4Me	**11a**
Ph	**11b**
$SiMe_3$	**11c**

Scheme 6.



11c **12**

Scheme 7.

ophilic attack at the nitrile ligand rather than giving substitution of the nitrile and formation of σ-alkynyl products [7, 8, 16a]. The reason is not attributable to the instability of the σ-alkynyl complexes because compounds of this type are known. In fact complexes $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(C{\equiv}CR)(Cp)_2]$ (R = *p*-C_6H_4Me, **11a**; R = Ph, **11b**; R = $SiMe_3$, **11c**) were obtained by deprotonation and acetylide deinsertion from the vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-C}(R)\text{=C(H)C=N(Me)(Xyl)}\}(\mu\text{-CO})(CO)(Cp)_2][SO_3CF_3]$ (R = Tol, Ph, $SiMe_3$) [22]. In the light of these considerations, we have investigated an alternative approach using acetone as labile ligand in place of nitriles, as it was successfully done in the case of $[Fe_2(\mu\text{-CNMe}_2)_2(CO)(Me_2C{=}O)(Cp)_2][SO_3CF_3]_2$ [5b]. Thus, the complex $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)_2(Cp)_2][SO_3CF_3]$ was treated with trimethylamine-N-oxide in acetone solution and, subsequently, reacted with $LiC{\equiv}CR$ (R = p-C_6H_4Me, Ph, $SiMe_3$) in THF, leading to the formation of the σ-alkynyl complexes **11a – c** (Scheme 6).

Compounds **11a – c** have been identified by comparison of the IR and ^{1}H NMR data with those reported in the literature [21]. The results described in Scheme 6 show a direct and efficient route to σ-coordinated alkynyl complexes which are by far less common [22] than the species with bridging alkynyl ligands [23]. Alkynyl complexes are of great interest for several potential applications such as non linear optics, luminescent materials, and molecular devices [24].

A final consideration concerns the reactivity of the complexes **11a – c**. These are relatively stable except **11c**, which appears to be very sensitive to hydrolysis. In particular, when chromatographed on alumina, with CH_2Cl_2 as eluent, compound **11c** is converted into the acyl complex $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)\{C(O)Me\}(Cp)_2]$ (**12**), in high yields (Scheme 7).

Compound **12** has been identified by spectroscopy and comparison with the data reported in literature for

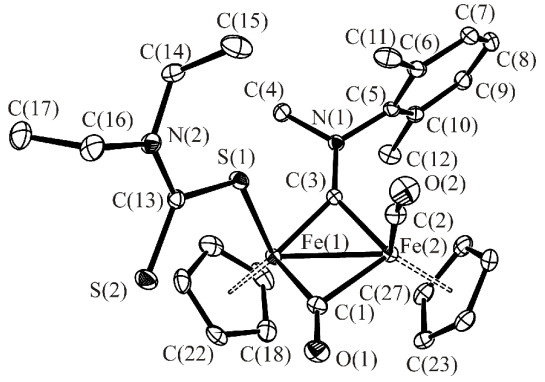


Fig. 1. ORTEP drawing of $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)\{SC(S)NEt_2\}(Cp)_2]$ (**5a**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are at the 30 % probability level.

analogous diiron aminocarbyne acyl-complexes [14]. Hydration of ruthenium-coordinated acetylides affording acyl derivatives is known [25], but usually requires strong acids (HBF_4, HOTf), whereas the reaction described in Scheme 7 occurs under surprisingly mild conditions.

*Description of the molecular structures of **5a**, **6a** and **8***

The structure models of the title compounds are shown in Figs. 1, 2 and 3. Selected details are compared in Table 1. The overall constitution is similar in the three species. The cyclopentadienyl ligands are in *cis* configuration and the dithiocarbamate (**5a**), diphenylphosphane (**6a**) and phenyl (**8**) ligands occupy equivalent terminal coordination sites. The molecules are necessarily asymmetric, and while the crystals of **5a** and **6a** are racemic, **8** contains homochiral molecules. A significant configurational difference is the orientation of the methyl and xylyl groups of the bridging aminocarbyne ligand. The bulkier xylyl is kept far from the dithiocarbamate and phenyl ligands in **5a** and **8**, respectively, but close with respect to the phosphane ligand in **6a**. A rationale of this feature is found in the almost parallel alignment of the

Table 1. Selected bond lengths (Å) and angles (deg) for $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)\{SC(S)NEt_2\}(Cp)_2]$ (**5a**), $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(PPh_2H)(Cp)_2][SO_3CF_3]$ (**6a**) and $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(Ph)(Cp)_2]$ (**8**).

	5a	**6a**	**8**
Fe(1)–Fe(2)	2.515(3)	2.515(1)	2.505(1)
Fe(1)–C(1)	1.856(2)	1.919(4)	1.832(7)
Fe(2)–C(1)	2.022(1)	1.946(4)	2.020(6)
C(1)–O(1)	1.174(2)	1.167(4)	1.172(7)
Fe(2)–C(2)	1.759(2)	1.758(4)	1.756(7)
C(2)–O(2)	1.147(2)	1.144(5)	1.146(7)
Fe(1)–C(3)	1.864(1)	1.880(3)	1.819(5)
Fe(2)–C(3)	1.871(1)	1.897(3)	1.899(5)
N(1)–C(3)	1.313(2)	1.302(4)	1.320(7)
N(1)–C(4)	1.478(2)	1.493(4)	1.484(7)
N(1)–C(5)	1.454(2)	1.457(4)	1.449(6)
Fe(1)–S(1)	2.274(1)	–	–
Fe(1)···S(2)	3.852(1)	–	–
Fe(1)–P(1)	–	2.197(1)	–
Fe(1)–C(Ph)	–	–	2.055(2)
Fe(1)–C(Cp)av	2.116	2.120	2.135
Fe(2)–C(Cp)av	2.116	2.125	2.133[a]
C(4)–N(1)–C(5)	113.1(1)	113.0(3)	114.0(4)
C(3)–N(1)–C(5)	123.5(1)	125.1(3)	123.1(4)
C(3)–N(1)–C(4)	123.0(1)	121.8(3)	122.8(4)
Fe(1)–C(3)–N(1)	136.7(1)	143.7(3)	140.7(4)
Fe(2)–C(3)–N(1)	138.6(1)	132.8(3)	134.4(4)
Fe(1)–C(1)–O(1)	147.8(1)	141.2(3)	147.3(5)
Fe(2)–C(2)–O(2)	130.7(1)	137.4(3)	131.4(5)

[a] Referred to the main image of the disordered Cp ligand (see Experimental Section).

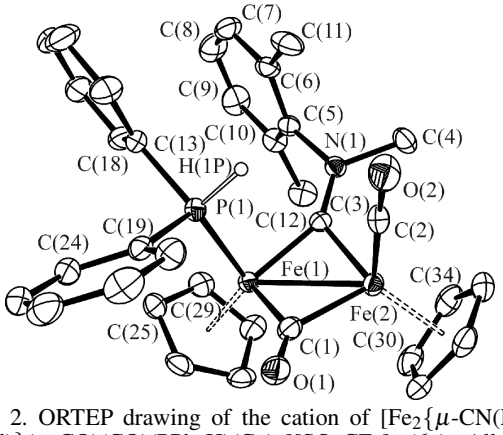


Fig. 2. ORTEP drawing of the cation of $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(PPh_2H)(Cp)_2][SO_3CF_3]$, (**6a**). All hydrogen atoms except the one attached to P(1) have been omitted for clarity Thermal ellipsoids are at the 30 % probability level.

xylyl plane with that of a phosphane phenyl group (interplanar angle *ca.* 8° and distance 3.36 Å). The ring overlap is partial but enough to establish a graphite-like π-π-stacking. In the common moieties of the three species the cation of **6a** shows some significant differences from the neutral molecules **5a** and **8**. In particular a marked asymmetry is observed in **5a** and **8** for the bridging carbonyl ligand [C(1)O(1)] with a shorter distance from the Fe(1) atom which bears the anionic ligand. The effect, although less pronounced, is observable also for the bridging aminocarbyne carbon atom [C(3)] and can be attributed to a good σ-donation to Fe(1) from the sulphur atom (**5a**) and phenyl group (**8**) that induces more pronounced back-donation to the bridging ligands with respect to Fe(2) bearing a terminal CO ligand. The bond asymmetry is less pronounced in **6a** in part because the neutral phosphane is less basic than the anionic ligands, but also because the delocalization of the cationic charge allows a better charge balance on the various atoms in **6a**.

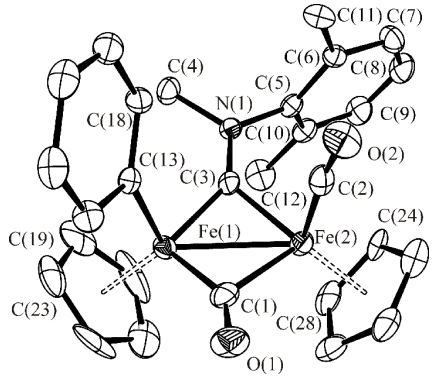


Fig. 3. ORTEP drawing of $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(Ph)(Cp)_2]$ (**8**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are at the 30 % probability level.

Conclusions

Displacement of the labile acetonitrile ligand in the diiron and diruthenium μ-aminocarbyne complexes **1**–**3** provides an effective route to the coordination of a variety of ligands: halides, phosphanes and dithiocarbamates. The latter exhibit an unusual η^1-coordination mode of the potentially bidentate S-ligand.

Conversely, substitution of nitriles by lithium organyls is restricted to LiPh and limited to the use of NC*t*Bu which does not contain acidic protons. The lack of general character of these substitution reactions is due to the prevalence of other reaction paths, including nucleophilic addition to the coordinated ligands. However, the use of acetone in place of nitriles as a labile ligand provides a successful route to the synthesis of σ-alkynyl complexes by reaction with lithium acetylides.

Experimental Section

Materials and measurements

All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of deactivated alumina (4 % w/w water). Glassware was oven-dried before use. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA instrument. ESI MS spectra were recorded on a Waters Micromass ZQ 4000 instrument with samples dissolved in CH_3CN. All NMR measurements were performed on Varian Gemini 300 and Mercury Plus 400 instruments. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. The spectra were fully assigned *via* DEPT experiments and ^1H-^{13}C correlation measured through gs-HSQC and gs-HMBC experiments [26]. Unless otherwise stated, NMR spectra were recorded at 298 K; NMR signals due to a second isomeric form (where applicable) are italicized. NOE measurements were recorded using the DPFGSE-NOE sequence [27]. All reagents were commercial products (Aldrich) of the highest purity available and used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. Compounds $[M_2\{\mu\text{-CN(Me)}(R)\}(\mu\text{-CO})(CO)(NCMe)(Cp)_2][SO_3CF_3]$ [*M* = Fe, *R* = Xyl, **1a**; *M* = Fe, *R* = Me, **1b**; *M* = Fe, *R* = CH_2Ph, **1c**; *M* = Ru, *R* = Xyl, **2a**; *M* = Ru, *R* = Me, **2b**] and $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(NC$*t*$Bu)(Cp)_2][SO_3CF_3]$ (**3**) were prepared by published methods [2a, 7a].

*Syntheses of $[Fe_2\{\mu\text{-CN(Me)}(R)\}(\mu\text{-CO})(CO)(X)(Cp)_2]$ (R = Me, X = Br, **4a**; R = Me, X = I, **4b**; R = CH_2Ph, X = Cl, **4c**; R = CH_2Ph, X = Br, **4d**; R = CH_2Ph, X = I, **4e**)*

Complex $[Fe_2\{\mu\text{-CN(Me)}_2\}(\mu\text{-CO})(CO)(NCMe)(Cp)_2][CF_3SO_3]$ (**1b**) (106 mg, 0.203 mmol), was dissolved in THF (15 mL) and treated with KBr (75 mg, 0.630 mmol) with stirring at r. t. for 12 h. Then, the mixture was chromatographed through alumina. An ochre yellow band, corresponding to compound **4a**, was collected using THF as eluent. Yield: 44 mg, 50 %. – $C_{15}H_{16}BrFe_2NO_2$ (433.89): calcd. C 41.52, H 3.72, N 3.23; found C 41.62, H 3.76, N 3.20. – IR (CH_2Cl_2): ν(CO) = 1978 (vs), *1958* (s), 1797 (s), $\nu(\mu$-CN) = 1574 (w) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = *4.74*, 4.66, *4.48*, 4.47 (s, 10 H, Cp), *4.76*, 4.50, *4.30*, 4.07 (s, 6 H, NMe); *cis*/*trans* ratio 2 : 1.

Complex **4a** was dissolved in CH_2Cl_2 and the solution was stirred for 6 h at reflux temperature. The mixture was filtered through alumina, and an ochre-yellow band, corresponding to *cis*-**4a** was collected, using THF as eluent.

Compounds **4b** – **e** were prepared by reacting **1b** – **c** with LiCl, KBr or KI, respectively, in boiling CH_2Cl_2 for 6 h. Successive work-up was analogous to that described for **4a**.

4b: Yield: 70 %; colour: brown. – $C_{15}H_{16}Fe_2INO_2$ (480.89): calcd. C 37.46, H 3.35, N 2.91; found C 37.54, H 3.38, N 2.82. – IR (CH_2Cl_2): ν(CO) = 1973 (vs), 1793 (s), $\nu(\mu$-CN) = 1567 (w) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 4.67, 4.54 (s, 10 H, Cp), 4.48, 4.17 (s, 6 H, NMe).

4c: Yield: 73 %; colour: brown. – $C_{21}H_{20}ClFe_2NO_2$(465.53): calcd. C 54.18, H 4.33, N 3.01; found C 54.27, H 4.38, N 3.03. – IR (CH_2Cl_2): ν(CO) = 1978 (vs), 1799 (s), $\nu(\mu$-CN) = 1529 (w) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.70 – 7.40 (m, 5 H, CH_2Ph), *6.77*, 5.94, 5.67 (d, 2 H, $^2J_{HH}$ = 14.7 Hz, C*H*$_2$Ph), *4.80*, 4.72, *4.61* (s, 10 H, Cp), 4.56, *4.09* (s, 3 H, NMe); isomer ratio 6 : 5. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 339.7, 339.2 (μ-C), 266.2, 265.5 (μ-CO), 212.0, 211.7 (CO), 136.0, 135.1 (*ipso*-Ph), 129.4 – 126.9 (CH_2*Ph*), 86.6, 86.5, 86.4, 86.2 (Cp), 70.1, 69.6 (*C*H$_2$Ph), 49.8, 48.9 (NMe).

4d: Yield: 87 %; colour: ochre yellow. – $C_{21}H_{20}BrFe_2NO_2$ (509.98): calcd. C 49.46, H 3.95, N 2.75; found C 49.40, H 4.02, N 2.66. – IR (CH_2Cl_2): ν(CO) = 1978 (vs), 1799 (s), $\nu(\mu$-CN) = 1534 (w) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.64 – 7.39 (m, 5 H, CH_2*Ph*), *4.83*, 4.76, *4.65* (s, 10 H, Cp), 4.08 (s, 3 H, NMe); isomer ratio 1 : 1. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 129.4, 128.3, 127.4, 127.0 (CH_2*Ph*), 86.6 (Cp).

4e: Yield: 70 %; colour: brown. – $C_{21}H_{20}Fe_2INO_2$ (556.98): calcd. C 45.28, H 3.62, N 2.51; found C 45.36, H 3.71, N 2.51. – IR (CH_2Cl_2): ν(CO) = 1974 (vs), 1793 (s), $\nu(\mu$-CN) = 1529 (w) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.64 – 7.39 (m, 5H, CH_2*Ph*), *6.74*, 5.92, 5.73, *5.69* (d, 2H, $^2J_{HH}$= 15 Hz, C*H*$_2$Ph), *4.80*, 4.72, 4.71, *4.60* (s, 10 H, Cp), 4.42, *4.08* (s, 3 H, NMe); isomer ratio 11 : 10. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 337.5, 337.4 (μ-C), 267.3, 267.0 (μ-CO), 214.7, 214.4 (CO), 135.8, 135.3 (*ipso*-Ph), 129.4 – 127.0 (CH_2*Ph*), 86.7, 86.6, 86.0, 85.8 (Cp), 71.9, 70.6 (*C*H$_2$Ph), 51.1, 50.4 (NMe).

*Syntheses of $[Fe_2\{\mu\text{-CN(Me)}(R)\}(\mu\text{-CO})(CO)\{SC(S)NEt\}_2(Cp)_2]$ (R = Xyl, **5a**; R = Me, **5b**)*

Complex **1a** (100 mg, 0.158 mmol), was dissolved in THF (15 mL) and treated with $NaSC(S)NEt_2$ (32 mg, 0.187 mmol) at reflux temperature for 45 min. Removal of the solvent and chromatography on alumina gave a red band, which was collected using a 1 : 1 mixture of CH_2Cl_2 and THF as eluent. **5a**: Yield: 74 mg, 79 %. – $C_{27}H_{32}Fe_2N_2O_2S_2$ (592.38): calcd. C 54.74, H 5.44, N 4.73; found C 54.81, H 5.36, N, 4.78. – IR (KBr pellets): ν = 1500 m (μ-CN), 1458 m (CN) cm^{-1}. – IR (CH_2Cl_2): ν(CO) = 1967 (vs), 1810 (s) cm^{-1}. – ^1H NMR ($CDCl_3$, 313 K): δ = 7.31 – 7.19 (m, 3 H, Me_2C_6*H*$_3$), 5.07, 4.28 (s, 10 H, Cp), 4.61 (s, 3 H, NMe), 3.72 (m br, 4 H, NCH_2), 2.69, 2.12 (s, 6 H, *Me*$_2C_6H_3$), 1.09, 0.91 (m, 6 H, NCH_2C*H*$_3$). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 313 K):

δ = 333.5 (μ-C), 259.8 (μ-CO), 213.7 (CO), 207.2 (SCS), 148.5 (*ipso*-$Me_2C_6H_3$), 133.3, 132.6, 130.9, 129.0, 126.9 ($Me_2C_6H_3$), 88.0, 85.7 (Cp), 51.7 (NMe), 46.9 (NCH_2), 18.6, 16.9 ($Me_2C_6H_3$), 12.7 (NCH_2CH_3).

Complex **5b** was prepared by the procedure described for **5a**, by reacting **1b** with $NaSC(S)NEt_2$. Crystals suitable for X-ray diffraction were obtained from a CH_2Cl_2 solution of **5a** layered with petroleum ether, at −20 °C.

5b: Yield: 69 %, colour: red. – $C_{20}H_{26}Fe_2N_2O_2S_2$ (502.25): calcd. C 47.83, H 5.22, N 5.58; found C 47.91, H 5.03, N 5.69. – IR (CH_2Cl_2): ν(CO) = 1966 (vs), 1810 (s), ν(μ-CN) = 1567 (w) cm^{-1}. – ^1H NMR ($CDCl_3$, 313 K): δ = 4.96, 4.71 (s, 10 H, Cp), 4.44, 4.15 (s, 6 H, NMe), 3.74 (m br, 4 H, NCH_2), 0.98 (m br, 6 H, NCH_2CH_3). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 313 K): δ = 333.9 (μ-C), 261.8 (μ-CO), 213.2 (CO), 208.3 (SCS), 87.3, 86.5 (Cp), 53.2, 50.9 (NMe), 46.9 (NCH_2), 12.2 (NCH_2CH_3).

*Syntheses of [Fe_2{μ-CN(Me)(R)}(μ-CO)(CO)(L)(Cp)$_2$][CF_3SO_3] (R = Xyl, L = PPh_2H, **6a**; R = Xyl, L = PPh_3, **6b**; R = Xyl, L = PMe_3, **6c**; R = Me, L = PMe_2Ph, **6d**; R = Me, L = PPh_3, **6e**; R = Me, L = $PMePh_2$, **6f**); and [Ru_2{μ-CN(Me)(R)}(μ-CO)(CO)(L)(Cp)$_2$][CF_3SO_3] (R = Xyl, L = PPh_2H, **6g**; R = Me, L = PPh_2H, **6h**)*

PPh_2H (0.42 mmol) was added to a solution of **1a** (147 mg, 0.232 mmol) in THF (15 mL), and the mixture was heated at reflux for 3 h. Then, the solvent was removed and the residue, dissolved in CH_2Cl_2, was chromatographed on alumina. The product **6a** was obtained as a dark brown fraction, using MeOH as eluent. Yield: 141 mg, 78 %. Crystals suitable for X-ray diffraction were obtained from a CH_2Cl_2 solution layered with diethyl ether, at −20 °C. – $C_{35}H_{33}NF_3Fe_2NO_5PS$ (779.36): calcd. C 56.94, H 4.24; found C 56.47, H 4.59. – IR (CH_2Cl_2): ν(CO) = 1979 (vs), 1809 (s), ν(μ-CN) = 1508 (m) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.72 – 7.19 (m, 13 H, Ph and $Me_2C_6H_3$), *5.30*, 5.04, *4.73*, 4.54 (s, 10 H, Cp), 4.95, *4.44* (d, 1 H, $^1J_{PH}$ = 359.7 Hz, PH), *4.37*, 4.05 (s, 3 H, NMe), *2.83*, 2.60, 2.03, *1.45* (s, 6 H, $Me_2C_6H_3$); isomer ratio = 2 : 1. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 331.7 (d, $^2J_{PC}$ = 16.2 Hz, μ-C), 262.3 (d, $^2J_{PC}$ = 18.0 Hz, μ-CO), 212.3 (d, $^3J_{PC}$ = 8.4 Hz, CO), 147.9 (*ipso*-$Me_2C_6H_3$), 132.4 – 127.7 (Ph and $Me_2C_6H_3$), *90.4*, 88.6, 88.0, *87.7* (Cp), 53.4 (NMe), 18.3, 17.5 ($Me_2C_6H_3$). – ^{31}P NMR ($CDCl_3$): δ = 55.4 (d, $^1J_{PH}$ = 359.7 Hz), *52.8* (d, $^1J_{PH}$ = 351.2 Hz).

Complexes **6b** – **h** were prepared by the procedure described for **6a**, by reacting **1a** – **b** and **2a** – **b** with the appropriate phosphine.

6b: Yield: 72 %; colour: brown. – $C_{41}H_{37}F_3Fe_2NO_5PS$ (855.46): calcd. C 57.56, H 4.36; found C 57.61, H 4.42. – IR (CH_2Cl_2): ν(CO) = 1985 (vs), 1797 (s) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.65 – 7.17 (m, 18 H, Ph and $Me_2C_6H_3$), *5.03*, 4.96, 4.52, *4.45* (s, 10 H, Cp), 4.54, *4.30* (s, 3 H, NMe), 2.73, *2.67*, *2.07*, 2.03 (s, 6 H, $Me_2C_6H_3$); isomer ratio 3 : 1. – ^{31}P NMR ($CDCl_3$): δ = 59.2, *57.7*.

6c: Yield: 78 %, colour: brown. – $C_{26}H_{30}NO_5F_3Fe_2PS$ (668.25): calcd. C 46.73, H 4.52; found C 46.92, H 4.29. – IR (CH_2Cl_2): ν(CO) = 1972 (vs), 1801 (s). – ^1H NMR ($CDCl_3$): δ = 7.26 (m, 3 H, $Me_2C_6H_3$), 4.97, 4.46 (s, 10 H, Cp), 4.36 (s, 3 H, NMe), 2.59, 2.12 (s, 6 H, $Me_2C_6H_3$), 1.22 (d, 9 H, $^2J_{PH}$ = 9.0 Hz, PMe_3). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 333.9 (d, $^2J_{PC}$ = 15.4 Hz, μ-C), 262.3 (d, $^2J_{PC}$ = 20.1 Hz, μ-CO), 214.8 (d, $^2J_{PC}$ = 3.0 Hz, CO), 147.9 (*ipso*-$Me_2C_6H_3$), 132.7, 132.0, 129.9, 129.0, 128.8 ($Me_2C_6H_3$), 88.3 (Cp), 54.8 (NMe), 18.8, 17.6 ($Me_2C_6H_3$), 18.1 (d, $^1J_{PC}$ = 34.9 Hz, PMe_3). – ^{31}P NMR ($CDCl_3$): δ = 26.3 (s).

6d: Yield: 80 %; colour: brown. – $C_{24}H_{27}F_3Fe_2NO_5PS$ (641.20): calcd. C 44.96, H 4.24; found C 45.06, H 4.16. – IR (CH_2Cl_2): ν(CO) = 1972 (vs), 1802 (s), ν(μ-CN) = 1573 (m) cm^{-1}. – ^1H NMR (CD_2Cl_2): δ = 7.40 – 7.12 (m, 5 H, Ph), 4.99 (s, 5 H, Cp), 4.65 (d, 5 H, $^3J_{PH}$ = 1.2 Hz, Cp), 4.14, 4.10 (s, 6 H, NMe), 1.30 (d, 3 H, $^2J_{PH}$ = 9.2 Hz, PMe), 1.20 (d, 3 H, $^2J_{PH}$ = 12.0 Hz, PMe). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 327.0 (d, $^2J_{PC}$ = 18.8 Hz, μ-C), 265.0 (d, $^2J_{PC}$ = 22.5 Hz, μ-CO), 214.8 (CO), 138.2 (*ipso*-Ph, $^1J_{PC}$ = 44 Hz), 130.9, 129.7 (Ph), 89.7, 88.9 (Cp), 54.9, 54.0 (NMe), 18.5 (d, $^1J_{PC}$ = 30.3 Hz, PMe), 16.9 (d, $^1J_{PC}$ = 30.3 Hz, PMe).

6e: Yield: 81 %; colour: brown. – $C_{34}H_{31}F_3Fe_2NO_5PS$ (765.34): calcd. C 53.36, H 4.08; found: C 53.51, H 4.12. – IR (CH_2Cl_2): ν(CO) = 1986 (vs), 1793 (s), ν(μ-CN) = 1572 (m) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.49 – 7.18 (m, 15 H, Ph), 5.07 (s, 5 H, Cp), 4.94 (d, 5 H, $^3J_{PH}$=1.4 Hz, Cp), 4.24, 4.14 (s, 6 H, NMe). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 328.5 (μ-C), 267.5 (μ-CO), 211.1 (CO), 134.5 (*ipso*-Ph, $^1J_{PC}$ = 42.0 Hz), 133.5, 131.6, 129.3 (Ph), 90.4, 89.0 (Cp), 56.4, 52.9 (NMe).

6f: Yield: 80 %; colour: dark green. – $C_{29}H_{29}F_3Fe_2NO_5PS$ (703.27): calcd. C 49.53, H 4.16; found C 49.51, H 4.10. – IR (CH_2Cl_2): ν(CO) = 1976 (vs), 1798 (s), ν(μ-CN) = 1567 (m) cm^{-1}. – ^1H NMR (CD_3CN): δ = 7.55 – 7.39 (m, 10 H, Ph), 5.12, 4.90 (s, 10 H, Cp), 4.18, 4.16 (s, 6 H, NMe), 1.51 (d, 3 H, $^2J_{PH}$ = 8.5 Hz, PMe).

6g: Yield: 85 %; colour: orange-yellow. – $C_{35}H_{33}NO_5F_3Ru_2PS$ (869.82): calcd. C 48.33, H 3.82; found C 48.37, H 3.76. – IR (CH_2Cl_2): ν(CO) = 1978 (vs), 1816 (s), ν(μ-CN) = 1519 (m) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 8.00 – 6.59 (m, 13 H, Ph and $Me_2C_6H_3$), 5.69, *5.44*, 5.10, *4.76* (s, 10 H, Cp), 5.34, *5.13* (d, 1 H, $^1J_{PH}$ = 360.6 Hz, PH), 4.16, *3.99* (s, 3 H, NMe), 2.53, *2.24*, 1.60, *1.20* (s, 6H, $Me_2C_6H_3$); isomer ratio 3 : 1. – ^{31}P NMR ($CDCl_3$): δ = 36.0 (d, $^1J_{PH}$ = 367.7 Hz).

6h: Yield: 82 %; colour: orange-yellow. – $C_{28}H_{27}NO_5F_3Ru_2PS$ (779.69): calcd. C 43.13, H 3.49; found C 43.21, H 3.42. – IR (CH_2Cl_2): ν(CO) = 1972 (vs), 1808 (s), ν(μ-CN) = 1592 (ms) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.87 – 7.26

(m, 10 H, Ph), 5.50, 5.34 (s, 10 H, Cp), 5.29 (d, 1H, $^1J_{PH}$ = 367.7 Hz, PH), 3.86, 3.27 (s, 6 H, NMe_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 298.8 (d, $^2J_{PC}$ = 11.3 Hz, μ-C), 237.5 (d, $^2J_{PC}$ = 11.9 Hz, μ-CO), 201.1 (d, $^3J_{PC}$ = 8.5 Hz, CO), 133.7 – 128.1 (Ph), 90.7, 90.1 (Cp), 54.3, 51.3 (NMe_2). – ^{31}P NMR ($CDCl_3$): δ = 36.0 (d, $^1J_{PH}$ = 367.7 Hz).

*Synthesis of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO){CH(CN)$_2$}(Cp)$_2$] (**7**)*

Compound **1a** (116 mg, 0.183 mmol), dissolved in THF (10 mL), was treated with a THF solution (1.0 mL) of $NaCH(CN)_2$ (0.34 mmol), freshly prepared from $CH_2(CN)_2$ and Na.

The mixture was stirred at reflux temperature for 20 min; then, the solvent was removed under vacuum. Chromatography of the residue on alumina afforded a green band (75 mg, 0.147 mmol), corresponding to **7**. Yield: 75 mg, 81 %. – $C_{25}H_{23}Fe_2N_3O_2$(509.16): calcd. C 58.97, H 4.55; found C 59.06, H 4.47. – IR (CH_2Cl_2): ν(C≡N) = 2214 m, ν(CO) = 1963 (vs), 1801 (s) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.36 – 7.07 (m, 3 H, $Me_2C_6H_3$), *4.83*, 4.82, 4.39, *4.27* (s, 10 H, Cp), *4.81*, 4.75 (s, 3 H, NMe), 2.67, 2.12 (s, 6 H, $Me_2C_6H_3$), *−1.24*, −1.35 (s, 1 H, $CHCN_2$), isomer ratio 18 : 1. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 337.5 (μ-C), 264.1 (μ-CO), 214.3 (CO), 149.1 (*ipso*-$Me_2C_6H_3$), 133.0, 132.1, 130.1, 128.6, 128.5 ($Me_2C_6H_3$), 124.5, 121.8 (CHCN), 88.6, 87.4 (Cp), 51.9 (NMe), 18.4, 17.5 ($Me_2C_6H_3$), −22.0 ($CHCN_2$).

*Reactions of **1a** with MeO$^-$/MeOH and EtO$^-$/EtOH*

Complex **1a** (90 mg, 0.142 mmol), dissolved in MeOH (10 mL), was treated at −30 °C, with a solution of NaOMe in MeOH (0.2 mL, 0.196 mmol), freshly prepared from MeOH and Na. The mixture was stirred for 2 h. Subsequently, the solvent was removed under reduced pressure and the residue was chromatographed on alumina. Elution with CH_2Cl_2 afforded a red band corresponding to [Fe$_2${μ-CN(Me)(Xyl)}(μ-H)(CO)$_2$(Cp)$_2$]. Yield: 38 mg, 60 %. Complex [Fe$_2${μ-CN(Me)(Xyl)}(μ-H)(CO)$_2$(Cp)$_2$] was also obtained by reacting respectively: **1a** with EtOH/EtONa (yield: 59 %), **3** with MeOH/MeONa (yield: 62 %), or **1a** with a saturated solution of Na_2CO_3 in MeOH (yield: 48 %).

*Synthesis of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO)(Ph)(Cp)$_2$] (**8**)*

A solution of **3** (108 mg, 0.160 mmol), dissolved in THF (15 mL), was cooled to −30 °C and treated with LiPh (0.21 mmol in cyclohexane/diethyl ether solution). The mixture was stirred for 2 h, then it was filtered through celite, and the solvent removed. Chromatography of the residue on alumina, using CH_2Cl_2 as eluent, afforded a dark green band, corresponding to **8**. Crystals suitable for X-ray diffraction were collected from a CH_2Cl_2 solution of **8** layered with petroleum ether, at −20 °C. Yield: 56 mg, 67 %. – $C_{28}H_{27}Fe_2NO_2$(521.21): calcd. C 64.52, H 5.22; found C 64.46, H 5.17. – IR (CH_2Cl_2): ν(CO) = 1958 (vs), 1775 (s), ν(μ-CN) = 1563 (w) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.50 – 6.55 (m, 8 H, $Me_2C_6H_3$ and Ph), 4.66, 4.13 (s, 10 H, Cp), 4.45 (s, 3 H, NMe), 2.57, 2.22 (s, 6 H, $Me_2C_6H_3$). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 340.8 (μ-C), 269.0 (μ-CO), 214.4 (CO), 156.1 – 121.6 ($Me_2C_6H_3$ and Ph), 89.3, 86.8 (Cp), 52.7 (NMe), 19.1, 18.6 ($Me_2C_6H_3$). – ESI-MS (ES^+): *m/z* (%) = 521 (27) $[M]^+$, 465 (100) $[M–2CO]^+$.

*Synthesis of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO)(PPh$_2$)(Cp)$_2$] (**9**)*

A solution of **3** (90 mg, 0.145 mmol) in THF (15 mL) was cooled to −30 °C and treated with $LiPPh_2$ (0.188 mmol), freshly generated from PPh_2H and *n*BuLi, in THF solution (2.0 mL). The mixture was stirred for 1 h, then the solvent was removed. Chromatography of the residue on alumina, using a 9 : 1 mixture of THF and MeOH as eluent, afforded an emerald green band, corresponding to **9**. Yield: 62 mg, 68 %. – $C_{34}H_{32}Fe_2NO_2P$ (629.29): calcd. C 64.89, H 5.13; found C 64.94, H 5.07. – IR (CH_2Cl_2): ν(CO) = 1981 (vs), 1786 (s), ν(μ-CN) = 1592 (m) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.72 – 7.22 (m, 16 H, $Me_2C_6H_3$ and PPh_2), *4.95*, 4.71, *4.42*, 4.25 (s, 10 H, Cp), 4.67 (s, 3 H, NMe), *2.69*, 2.64, 2.23 (s, 6 H, $Me_2C_6H_3$). Isomer ratio 3 : 1. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 333.0 (μ-C), 267.6 (μ-CO), *213.1*, 212.0 (CO), 151.0 – 125.6 (Ph and $Me_2C_6H_3$), 89.0, *87.4*, *87.3*, 87.0 (Cp), 51.4 (NMe), 18.6, *18.5*, *18.4*, 18.2 ($Me_2C_6H_3$). – ^{31}P NMR ($CDCl_3$): δ = 34.7, *33.6*.

*Synthesis of [Fe$_2${C(Me)N(Me)(Xyl)}(μ-CO)$_2$(CO)(Cp)$_2$] (**10**)*

A solution of **1a** (100 mg, 0.148 mmol) in THF (10 mL) was cooled to −30 °C and treated with LiMe (0.17 mmol in 0.17 mL of a diethyl ether solution). The mixture was stirred for 2 h, then it was filtered though alumina. Subsequently, the residue was chromatographed on alumina and a dark green band was collected using THF as eluent. Yield: 26 mg, 36 %. – $C_{24}H_{25}Fe_2NO_3$(487.15): calcd. C 59.17, H 5.17, N 2.88; found C 59.04, H 5.05, N 2.74. – IR (CH_2Cl_2): ν(CO) 1932 (vs), 1710 (vs) cm^{-1}. – ^1H NMR ($CDCl_3$) 7.32 – 7.15 (m, 3 H, $Me_2C_6H_3$), 4.93 (s, 3 H, NMe), 4.77, 4.31 (s, 10 H, Cp), 2.05, 1.94 (s, 6 H, $Me_2C_6H_3$), 1.72 (s, 3 H, FeC*Me*). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 288.6 (μ-CO), 275.5 (Fe*C*Me), 130.1 – 128.6 ($Me_2C_6H_3$), 88.6, 87.8 (Cp), 49.4 (NMe), 38.3 (FeC*Me*), 18.3, 17.6 ($Me_2C_6H_3$).

*Syntheses of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO)(C≡CR)(Cp)$_2$] (R = Tol, **11a**; R = Ph, **11b**; R = SiMe$_3$, **11c**)*

Complex [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO)$_2$(Cp)$_2$][CF_3SO_3] (100 mg, 0.161 mmol) was dissolved in acetone

Compound	**5a**	**6a**	**8**
Formula	$C_{27}H_{32}Fe_2N_2O_2S_2$	$C_{35}H_{33}F_3Fe_2NO_5PS$	$C_{28}H_{27}Fe_2NO_2$
M	592.37	779.35	521.21
T [K]	293(2)	293	293
Crystal size [mm^3]	$0.35 \times 0.30 \times 0.25$	$0.28 \times 0.22 \times 0.15$	$0.25 \times 0.23 \times 0.20$
λ [Å]	0.71073	0.71073	0.71073
Crystal symmetry	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1$
a [Å]	10.3866(7)	8.614(2)	8.6784(3)
b [Å]	18.613(1)	24.598(5)	13.7074(5)
c [Å]	14.0915(9)	15.629(3)	9.9854(3)
β [deg]	96.546(1)	92.57(3)	97.024(2)
Cell volume [Å^3]	2706(3)	3308(1)	1178.93(7)
Z	4	4	2
D_c [Mg m^{-3}]	1.454	1.565	1.468
μ(MoK_α) [mm^{-1}]	1.253	1.050	1.256
F(000) [e]	1232	1600	540
θ limits [deg]	1.82 – 30.01	1.54 – 25.03	2.05 – 28.00
Reflections collected	34442	28825	14370
Unique obs. reflections ($F_o \geq 4\sigma(F_o)$)	7880	5849	5686
R_{int}	0.0371	0.0687	0.0668
Goodness-of-fit-on F^2	1.046	1.038	1.016
$R1$ (F)[a], $wR2$ (F^2)b	0.0299, 0.0745	0.0446, 0.1136	0.0543, 0.1122
Absolute structure parameter x	–	–	0.05(3)
Largest diff. peak and hole [e Å^{-3}]	0.530 / −0.623	0.405 / −0.520	0.507 / −0.392

Table 2. Crystal data and experimental details for complexes **5a**, **6a** and **8**.

[a] $R1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$.
[b] $wR2 = [\Sigma w(F_o^2 - F_c^2)2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

(15 mL) and treated with Me_3NO (17 mg, 0.227 mmol). The mixture was stirred for 30 min and filtered on a celite pad. The volatile material was removed *in vacuo*. The residue was dissolved in THF (15 mL) and treated, at −30 °C, with a THF solution of LiC≡CTol (2.0 mL, 0.15 mmol), freshly prepared from HC≡CTol and *n*BuLi. The mixture was allowed to warm to r. t., stirred for an additional 40 min and then filtered through a celite pad. Removal of the solvent gave a yellow residue which was washed with petroleum ether (2 × 20 mL) to afford **11a**. Complex **11b – c** were obtained by the same procedure described for **11a**, by reacting **12** with LiC≡CPh and LiC≡CSiMe$_3$, respectively.

*Synthesis of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO){C(O)Me}(Cp)$_2$] (**12**)*

Complex **11c** (75 mg, 0.139 mmol) was chromatographed on an alumina column (2 × 8 cm) with CH_2Cl_2 as eluent. A green band was collected and yielded **12** as a green powder upon removal of the solvent under reduced pressure. Yield: 57 mg, 84 %. – $C_{24}H_{25}Fe_2NO_3$(487.15): calcd. C 59.17, H 5.17, N 2.88; found C 59.16, H 5.20, N 2.79. – IR (CH_2Cl_2): ν(CO) = 1962 (vs), 1773 (s), 1597 (ms) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 7.33 – 7.18 (m, 3 H, $Me_2C_6H_3$), 4.84, 4.24 (s, 10 H, Cp), 4.30 (s, 3 H, NMe), 2.56, 2.44 (s, 6 H, $Me_2C_6H_3$and C{O}Me), 2.29 (s, 3 H, $Me_2C_6H_3$). – ^{13}C NMR ($CDCl_3$): δ = 335.5 (μ-C), 270.3, 268.0 (μ-CO and *C*{O}Me), 213.5 (CO), 147.6 (*ipso*-$Me_2C_6H_3$), 134.3, 132.4, 129.3, 127.2 ($Me_2C_6H_3$), 87.9, 85.3 (Cp), 51.0 (NMe), 45.9 (C{O}*Me*), 17.7, 16.7 ($Me_2C_6H_3$).

*X-Ray crystallography for **5a**, **6a** and **8***

The diffraction experiments were carried out at r. t. on a Bruker AXS SMART 2000 CCD based diffractometer using graphite monochromated MoK_α radiation (λ = 0.71073 Å). Intensity data were measured over the full diffraction sphere using 0.3° wide ω scans and a crystal-to-detector distance of 5.0 cm. The software SMART [28] was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by software SAINT [28] and an empirical absorption correction was applied with SADABS [29]. The structures were solved by direct methods (SIR97) [30] and subsequent Fourier syntheses, and refined by full-matrix least-squares calculations on F^2 (SHELXTL) [31] attributing anisotropic thermal parameters to all non-hydrogen atoms. In complex **8**, the Cp ligand bound to Fe(2) was found disordered over two positions and the site occupation factors were refined yielding the values 0.60 and 0.40, respectively. The methyl, methylene and arene hydrogen atoms were placed in calculated positions and refined with idealized geometry, whereas the H atom attached to P(1) in **6a** was located in the Fourier map and refined isotropically. The racemic mixture of complex **8** crystallized as a conglomerate of chiral crystals in the space group $P2_1$ for which the absolute structure was determined. Further details of data collection and refinement are listed in Table 2.

CCDC 625083 (**5a**), CCDC 625084 (**6a**) and CCDC 625085 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge

from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) R. A. Michelin, M. Mozzon, R. Bertani, *Coord. Chem. Rev.* **1996**, *147*, 299 – 338; b) V. Y. Kukushkin, A. J. L. Pombeiro, *Chem. Rev.* **2002**, *102*, 1771 – 1802.

[2] a) V. G. Albano, L. Busetto, M. Monari, V. Zanotti, *J. Organomet. Chem.* **2000**, *606*, 163 – 168; b) L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *J. Braz. Chem. Soc.* **2003**, *14*, 902 – 907.

[3] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Inorg. Chim. Acta* **2005**, *358*, 1204 – 1216.

[4] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, E. Zoli, *J. Organomet. Chem.* **2005**, *690*, 348 – 357.

[5] a) K. Boss, M. G. Cox, C. Dowling, A. R. Manning, *J. Organomet. Chem.* **2000**, *61*, 18 – 35; b) K. Boss, C. Dowling, A. R. Manning, *J. Organomet. Chem.* **1996**, *509*, 197 – 207.

[6] a) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *Organometallics* **2003**, *22*, 1326 – 1331; b) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *J. Organomet Chem.* **2004**, *689*, 528 – 538.

[7] a) V. G. Albano, S. Bordoni, L. Busetto, F. Marchetti, M. Monari, V. Zanotti, *J. Organomet. Chem.* **2003**, *684*, 37 – 43; b) L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Eur. J. Inorg. Chem.* **2004**, 1494 – 1504.

[8] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, E. Zoli, *J. Organomet. Chem.* **2005**, *690*, 1959 – 1970.

[9] a) V. G. Albano, S. Bordoni, L. Busetto, A. Palazzi, P. Sabatino, V. Zanotti, *J. Organomet. Chem.* **2002**, *659*, 15 – 21; b) W.-F. Liaw, J.-H. Lee, H.-B. Gau, C.-H. Chen, S.-J. Jung Hung, C.-H. Hu, *J. Am. Chem. Soc.* **2002**, *124*, 1680 – 1688; c) G. Exarchos, S. D. Robinson, J. W. Steed, *Polyhedron* **2001**, *20*, 2951 – 2963.

[10] See for example: a) C. Landgrafe, W. S. Sheldrick, *J. Chem. Soc., Dalton Trans.* **1994**, 1885 – 1893; b) L. H. Pignolet, S. H. Wheeler, *Inorg. Chem.* **1980**, *19*, 935 – 940; c) R. E. Marsh, *Acta Crystallogr., Sect. B: Struct. Sci.* **1997**, *53*, 317 – 322.

[11] a) B. H. Chen, Y. Z. Li, Y. X. Ma, X. L. Wu, P. R. Li, *Acta Crystallog.* **2003**, *E59*, m223–m224; b) E. Roman, D. Catheline, D. Astruc, P. Batail, L. Ouahab, F. J. Varret, *J. Chem. Soc., Chem. Comm.* **1982**, *2*, 129 – 131; c) S. Y. Ho, E. R. T. Tiekink, *Acta Crystallogr., Sect. E: Struct. Rep.* **2002**, *58*, m86–m87; d) C. S. Lai, E. R. T. Tiekink, *Appl. Organomet. Chem.* **2003**, *17*, 141 – 142.

[12] E. J. Fernandez, J. M. Lopez de Luzuriaga, M. Monge, E. Olmos, A. Laguna, M. D. Villacampa, P. G. Jones, *J. Cluster Sci.* **2000**, *11*, 153 – 167.

[13] a) M. Bardaji, A. Blasco, J. Jimenez, P. G. Jones, A. Laguna, M. Laguna, F. Merchan, *Inorg. Chim. Acta* **1994**, *223*, 55 – 61; b) M. M. Kubicki, R. Kergoat, J. E. Guerchais, R. Mercier, J. Douglade, *J. Cryst. Mol. Struct.* **1981**, *11*, 43 – 45.

[14] V. G. Albano, L. Busetto, C. Camiletti, C. Castellari, M. Monari, V. Zanotti, *J. Chem. Soc., Dalton Trans.* **1997**, 4671 – 4676.

[15] L. Busetto, C. Camiletti, V. Zanotti, V. G. Albano, P. Sabatino, *J. Organomet. Chem.* **2000**, *593 – 594*, 335 – 341.

[16] a) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, V. Zanotti, *J. Organomet Chem.* **2002**, *649*, 64 – 69; b) B. T. Sterenberg, R. W. Hilts, G. Moro, R. McDonald, M. Cowie, *J. Am. Chem. Soc.* **1995**, *117*, 245 – 258.

[17] a) E. Bill, V. Schunemann, A. X. Trautwein, R. Weiss, J. Fischer, A. Tabard, R. Guilard, *Inorg. Chim. Acta* **2002**, *339*, 420 – 426; b) D. Huang, W. E. Streib, J. C. Bollinger, K. C. Caulton, R. F. Winter, T. Scheiring, *J. Am. Chem. Soc.* **1999**, *121*, 8087 – 8097; c) T. A. Bazhenova, L. M. Kachapina, A. E. Shilov, M. Y. Antipin, Y. T. Struchkov, *J. Organomet. Chem.* **1992**, *428*, 107 – 123; d) J. M. Jefferis, G. S. Girolami, *Organometallics* **1998**, *17*, 3630 – 3632.

[18] a) T. E. Bitterwolf, J. L. Haener, J. E. Shade, A. L. Rheingold, G. P. A. Yap, *J. Organomet. Chem.* **1997**, *547*, 23 – 33; b) P. Briard, J. A. Cabeza, A. Llamazares, L. Ouahab, V. Riera, *Organometallics* **1993**, *12*, 1006 – 1008; c) M. I. Bruce, P. A. Humphrey, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1996**, *526*, 85 – 97; d) A. R. Chakravarty, F. A. Cotton, D. A. Tocher, *J. Am. Chem. Soc.* **1984**, *106*, 6409 – 6413; e) F.-S. Kong, W.-T. Wong, *J. Chem. Soc., Dalton Trans.* **1999**, 2497 – 2510.

[19] J. A. Cabeza, R. J. Franco, A. Llamazares, V. Riera, E. Perez-Carreno, J. F. Van der Maelen, F. Juan, *Organometallics* **1994**, *13*, 55 – 59.

[20] V. Zanotti, S. Bordoni, L. Busetto, L. Carlucci, A. Palazzi, R. Serra, V. G. Albano, M. Monari, F. Prestopino, F. Laschi, P. Zanello, *Organometallics* **1995**, *14*, 5232 – 5241.

[21] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Organometallics* **2005**, *24*, 2297 – 2306.

[22] S. K. Hurst, T. Ren, *J. Organomet Chem.* **2003**, *670*, 188 – 197.

[23] a) H. Lang, D. S. A. George, G. Rheinwald, *Coord. Chem. Rev.* **2000**, *206 – 207*, 101 – 197; b) R. Nast, *Coord. Chem. Rev.* **1982**, *47*, 89 – 124; c) A. A. Cherkas, L. H. Randall, N. J. Taylor, G. N. Mott, J. E. Yule, J. L. Guinamant, A. J. Carty, *Organometallics* **1990**, *9*, 1677 – 1685; d) S. A. G. Darren, R. McDonald, M. Cowie, *Organometallics* **1998**, *17*, 2553 – 2566; e) G. Hogarth, S. P. Redmond, *J. Organomet. Chem.* **1997**, *534*, 221 – 227; f) W. F. Smith, J. Yule, N. J. Taylor, H. N. Paik, A. J. Carty, *Inorg. Chem.* **1977**, *16*, 1593 – 1600.

[24] a) N. J. Long, C. K. Williams, *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 2586 – 2617; b) I. R. Whittall, A. M. McDonagh, M. G. Humphrey, M. Samoc, *Adv. Organomet. Chem.* **1998**, *42*, 291 – 362; c) V. W. W. Yam, *Acc. Chem. Res.* **2002**, *35*, 555 – 563; d) R. Ziessel, M. Hissler, A. El-Ghayoury, A. Harriman, *Coord. Chem. Rev.* **1998**, *180*, 1251 – 1298; e) F. Paul, C. Lapinte, *Coord. Chem. Rev.* **1998**, *178 – 180*, 431 – 509.

[25] a) Y. Arikawa, Y. Nishimura, H. Kawano, M. Onishi, *Organometallics* **2003**, *22*, 3354 – 3356; b) C. Menendez, D. Morales, J. Perez, V. Riera, D. Miguel, *Organometallics* **2001**, *20*, 2775 – 2781.

[26] W. Wilker, D. Leibfritz, R. Kerssebaum, W. Beimel, *Magn. Reson. Chem.* **1993**, *31*, 287 – 292.

[27] K. Stott, J. Stonehouse, J. Keeler, T. L. Hwang, A. J. Shaka, *J. Am. Chem. Soc.* **1995**, *117*, 4199 – 4200.

[28] SMART & SAINT Software Reference Manuals, version 5.051 (Windows NT Version), Bruker Analytical X-ray Instruments Inc., Madison, WI (USA) **1998**.

[29] G. M. Sheldrick, SADABS, program for empirical absorption correction, University of Göttingen, Göttingen (Germany) **1996**.

[30] A. Altomare, M. C. Burla, M. Cavalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* **1999**, *32*, 115 – 119.

[31] G. M. Sheldrick, SHELXTL*plus* Version 5.1 (Windows NT version) Structure Determination Package; Bruker Analytical X-ray Instruments Inc., Madison, WI (USA) **1998**.