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

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Z. Naturforsch. **2007**, *62b,* 427 – 438; received November 2, 2006

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