

**Tri(1-cyclohepta-2,4,6-trienyl)-phosphane,  $P(C_7H_7)_3$ , as a Tripodal Tetradentate Ligand in Cationic, Five-coordinate Complexes of Platinum(II) and Palladium(II)**

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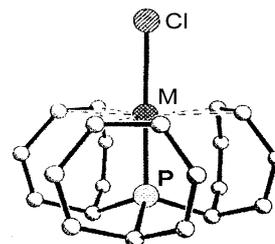
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Platinum, Palladium, Olefinic Phosphanes

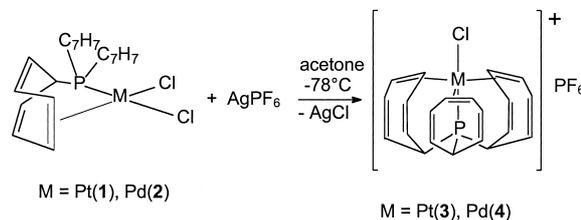
Chloride abstraction, using  $AgPF_6$ , from tri(1-cyclohepta-2,4,6-trienyl)phosphane platinum and palladium dichloride,  $[P]MCl_2$  [ $M = Pt$  (1),  $Pd$  (2)], affords the complexes  $\{[P]MCl\}PF_6$  [ $M = Pt$  (3),  $Pd$  (4)] in good yields. The central metal is coordinated by the chloro ligand, the phosphorus atom and by three  $\eta^2-C=C$  units, one of each  $C_7H_7$  ring. This assignment of a highly symmetrical  $C_{3v}$  structure is based on a consistent set of NMR data ( $^1H$ ,  $^{13}C$ ,  $^{31}P$ ,  $^{195}Pt$  NMR), in agreement with NMR data of the corresponding known neutral iridium and rhodium complexes  $[P]MCl$  [ $M = Ir$  (5),  $Rh$  (6)]. The chemical shift  $\delta^{103}Rh$  of 6 was determined, and a nearly linear relationship  $\delta^{195}Pt / \delta^{103}Rh$  was established.

Tripodal polyphosphane ligands such as tri(2-diorganylphosphano-ethyl)phosphane,  $P(CH_2CH_2-PR_2)_3$ , are known to stabilize the coordination number five in the chemistry of late transition metals including iridium, rhodium, platinum and palladium [1,2]. We have recently studied the coordination chemistry of tri(1-cyclohepta-2,4,6-trienyl)phosphane,  $P(C_7H_7)_3$  ( $[P]$  when coordinated to a metal) [3], which can act as a tripodal tetradentate ligand if each of the central  $C=C$  double bonds of the three  $C_7H_7$  rings coordinates  $\eta^2$  to a metal center in addition to the P-metal bond. This situation has been found in the neutral complexes  $[P]IrCl$  (5) and  $[P]RhCl$  (6) (Scheme 1) [4], and we now describe the hexafluorophosphate salts 3 and 4 of the isoelectronic cations,  $\{[P]PtCl\}^+$  and  $\{[P]PdCl\}^+$ , respectively.



Scheme 1.  $M = Ir$  (5),  $Rh$  (6); an X-ray structural analysis was carried out for 6 [4].

The chlorides  $[P]MCl_2$  [5] [ $M = Pt$  (1) and  $M = Pd$  (2)] have already been used as versatile starting complexes for the synthesis of derivatives with  $[P]Pt$  and  $[P]Pd$  core [5–9]. Scheme 2 summarizes the results of the reactions of 1 and 2 with  $AgPF_6$ , leading to the hexafluorophosphates  $\{[P]MCl\}PF_6$  [ $M = Pt$  (3) and  $M = Pd$  (4)]. The tetrafluoroborates can be prepared in the same way; however, their solubility is lower and their purification is more difficult. The complexes 3 and 4 are yellow or violet powders, respectively, which are stable on air and moderately soluble in polar solvents such as acetone or  $CH_2Cl_2$ . So far we have not succeeded in obtaining suitable single crystals for an X-ray analysis. Therefore, the characterization of both 3 and 4 has to be based mainly on NMR spectroscopic data in solution.



Scheme 2. Synthesis of  $\{[P]MCl\}PF_6$ .

The appearance of the  $^1H$  and  $^{13}C$  NMR spectra of the platinum and palladium complexes 3 and 4 (Table 1) is similar to those of the iridium and rhodium counterparts 5 and 6, although there are differences in the  $^1H$  and  $^{13}C$  nuclear shielding which can be ascribed at least in part ( $\delta^1H$  values) to the ionic character of 3 and 4 and the different interaction with the solvent. The magnitude of the coupling constants  $^nJ(^{31}P, ^1H)$  and  $^nJ(^{31}P, ^{13}C)$  is, however, comparable. On the other hand, as expected, the magnitude of coupling constants involving  $^{195}Pt$ , such as  $^nJ(^{195}Pt, ^1H)$ ,  $^nJ(^{195}Pt, ^{13}C)$

Table 1.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{195}\text{Pt}$  NMR data of the complexes  $\{[\text{P}]\text{MCl}\}\text{PF}_6$  [ $\text{M} = \text{Pt}$  (3),  $\text{Pd}$  (4)] and of  $[\text{P}]\text{MCl}$  [ $\text{M} = \text{Ir}$  (5),  $\text{Rh}$  (6)] [4,10] for comparison <sup>a</sup>.

	$\{[\text{P}]\text{PtCl}\}\text{PF}_6$ (3)	$\{[\text{P}]\text{PdCl}\}\text{PF}_6$ (4)	$[\text{P}]\text{IrCl}$ (5)	$[\text{P}]\text{RhCl}$ (6)
$\delta^1\text{H}$ <sup>b</sup>				
$\text{H}^1$	3.60 (dt, 3H) (8.3) [11.8]	3.77 (dt, 3H) (8.5) [9.2]	1.95	1.94 (dt, 3H) (8.1) [12.0]
$\text{H}^{2,7}$	6.54 (m, 6H) [11.7]	6.49 (m, 6H) [12.9]	5.69	6.00 (m, 6H)
$\text{H}^{3,6}$	6.45 (m, 6H) [8.3]	6.66 (m, 6H) [8.8]	5.87	5.86 (m, 6H)
$\text{H}^{4,5}$	6.37 (d, 6H) [3.4] [49.0]	7.13 (m, 6H)	4.81	5.45 (m, 6H)
$\delta^{13}\text{C}$ <sup>c</sup>				
$\text{C}^1$	36.5 (d) [22.0] [12.0]	43.9 (d) [13.4]	31.1 [23.9]	35.9 (d) [16.9]
$\text{C}^{2,7}$	132.1 (d) [4.3] [35.9]	131.52 (d) [3.2]	125.1 [2.2]	124.9 (s)
$\text{C}^{3,6}$	130.3 (d) [8.3] [26.5]	131.47 (d) [8.1]	131.1 [7.8]	131.9 (d) [7.7]
$\text{C}^{4,5}$	92.7 (s) {61.4}	110.6 (s)	65.4 (s)	80.9 (d) {6.3}
$\delta^{31}\text{P}$ <sup>d</sup>	353.1 (s) {4048} -143.1 (sept) $[\text{PF}_6]^-$ <709>	435.9 (s) -143.0 (sept) $[\text{PF}_6]^-$ <708>	265.2	325.3 (d) $^1J(^{103}\text{Rh}, ^{31}\text{P}) = 189.5$ Hz
	$\delta^{195}\text{Pt}$ -462.6 (d) {4048}	-	-	$\delta^{103}\text{Rh}$ -355 (d)

<sup>a</sup> Measurements of 3 and 4 in acetone- $d_6$  at 25 °C; 5 and 6 in  $\text{CDCl}_3$ .

<sup>b</sup> ( ) / [ ] / { } coupling constants  $^3J(^1\text{H}, ^1\text{H})$  /  $^nJ(^{31}\text{P}, ^1\text{H})$  /  $^2J(^{195}\text{Pt}, ^1\text{H})$  in Hz.

<sup>c</sup> [ ] / { } coupling constants  $^nJ(^{31}\text{P}, ^{13}\text{C})$  /  $^nJ(^{195}\text{Pt}, ^{13}\text{C})$  in Hz.

<sup>d</sup> { } / < > coupling constants  $^1J(^{195}\text{Pt}, ^{31}\text{P})$  /  $^1J(^{31}\text{P}, ^{19}\text{F})$  in Hz.

and  $^1J(^{195}\text{Pt}, ^{31}\text{P})$ , is much larger (by a factor of approximately 10–20 due to small  $\gamma(^{103}\text{Rh})$  and the differing valence s electron densities of  $^{195}\text{Pt}$  and  $^{103}\text{Rh}$ ) than that of the corresponding cou-

pling constants involving  $^{103}\text{Rh}$ . Fig. 1 shows a typical  $^{13}\text{C}$  NMR spectrum of 3. The 2D  $^1\text{H}/^1\text{H}$  COSY (not shown) and the 2D  $^{13}\text{C}/^1\text{H}$  HETCOR experiment (Fig. 2) confirm the mutual assignment of  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals. In addition, the relative signs of numerous coupling constants become available by analyzing the tilt of the cross peaks [11], where a positive or a negative tilt indicates alike or opposite signs, respectively, of the coupling constants. The results (Fig. 2) are in agreement with those for  $\{[\text{P}]\text{PtCp}\}^+$  [6].

Remarkably, the  $^{31}\text{P}$  nuclear shielding in 3 ( $\delta^{31}\text{P}$  353.1) and 4 ( $\delta^{31}\text{P}$  435.9) is even further reduced when compared with that in  $[\text{P}]\text{IrCl}$  (5) ( $\delta^{31}\text{P}$  265.2) and  $[\text{P}]\text{RhCl}$  (6) ( $\delta^{31}\text{P}$  325.3). The low  $^{31}\text{P}$  nuclear shielding in these complexes is typical of the coordination to the metal by phosphorus and three  $\eta^2\text{-C}=\text{C}$  units of  $\text{P}(\text{C}_7\text{H}_7)_3$  [4,10]. This deshielding is most likely the result of steric constraints in the molecular structures by which the  $^{31}\text{P}$  nucleus is kept in a distinct position with respect to the non-coordinated  $\text{C}=\text{C}$  bonds, reminding of  $^{31}\text{P}$  nuclear deshielding effects observed for 7-phospha-norbornadiene derivatives [11]. The  $\delta^{31}\text{P}$  values cannot be explained by assuming a fast exchange of the  $\text{C}_7\text{H}_7$  rings in  $\eta^2\text{-C}=\text{C}$  coordination to the metal. If only one or two  $\text{C}_7\text{H}_7$  rings on average would be linked to the metal, the  $^{31}\text{P}$

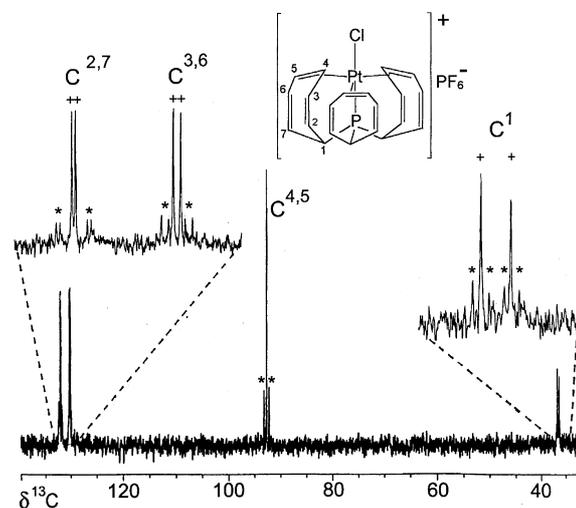


Fig. 1.  $^{13}\text{C}$  NMR spectrum of  $\{[\text{P}]\text{PtCl}\}\text{PF}_6$  (3) (in acetone- $d_6$  at 25 °C). All  $\text{C}_7\text{H}_7$  rings are equivalent as shown by the four  $^{13}\text{C}$  resonance signals, split due to  $^{31}\text{P}$ - $^{13}\text{C}$  coupling (marked by +), and accompanied by  $^{195}\text{Pt}$  satellites due to  $^nJ(^{195}\text{Pt}, ^{13}\text{C})$  (marked by \*).

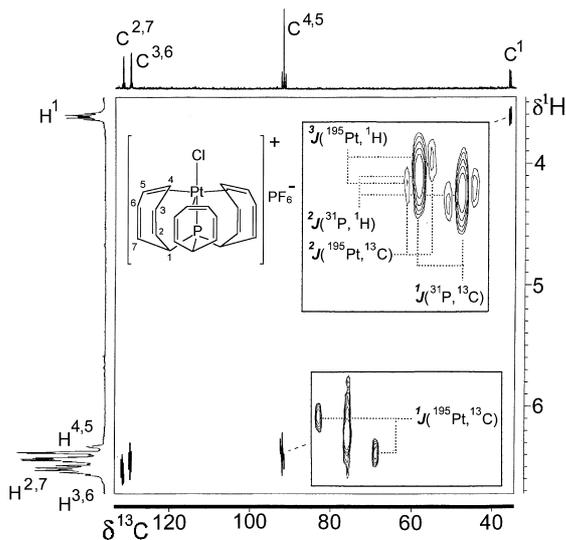


Fig. 2. Contour plot of the 2D  $^{13}\text{C}/^1\text{H}$  HETCOR NMR experiment of  $\{[\text{P}]\text{PtCl}\}\text{PF}_6$  (**3**) (in acetone- $d_6$  at 25 °C). The tilt of relevant cross peaks (some are shown in expansions) provide the following relative coupling signs, where  $> 0$  means positive tilt and alike signs, while  $< 0$  means negative tilt and opposite signs [14]:  $(\text{H}/\text{C})^1 \rightarrow {}^1J(^{31}\text{P}, ^{13}\text{C}^1) / {}^2J(^{31}\text{P}, ^1\text{H}^1) < 0$ ;  ${}^2J(^{195}\text{Pt}, ^{13}\text{C}^1) / {}^3J(^{195}\text{Pt}, ^1\text{H}^1) > 0$ ;  $(\text{H}/\text{C})^{2,7} \rightarrow {}^2J(^{31}\text{P}, ^{13}\text{C}^{2,7}) / {}^3J(^{31}\text{P}, ^1\text{H}^{2,7}) < 0$ ;  ${}^3J(^{195}\text{Pt}, ^{13}\text{C}^{2,7}) / {}^4J(^{195}\text{Pt}, ^1\text{H}^{2,7}) < 0$ ;  $(\text{H}/\text{C})^{3,6} \rightarrow {}^3J(^{31}\text{P}, ^{13}\text{C}^{3,6}) / {}^4J(^{31}\text{P}, ^1\text{H}^{3,6}) < 0$ ;  ${}^2J(^{195}\text{Pt}, ^{13}\text{C}^{3,6}) / {}^3J(^{195}\text{Pt}, ^1\text{H}^{3,6}) < 0$ ;  $(\text{H}/\text{C})^{4,5} \rightarrow {}^1J(^{195}\text{Pt}, ^{13}\text{C}^{4,5}) / {}^2J(^{195}\text{Pt}, ^1\text{H}^{4,5}) < 0$ .

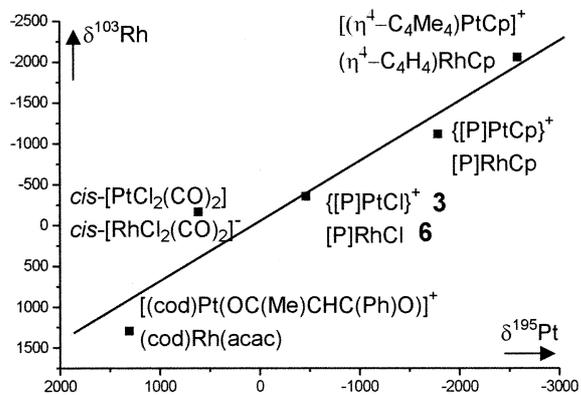


Fig. 3. Linear regression of some  $\delta^{195}\text{Pt}$  and  $\delta^{103}\text{Rh}$  data for isostructural Pt(II) and Rh(I) complexes:  $\delta^{103}\text{Rh} = -14 (\pm 173.5) + 0.75 (\pm 0.11) (\delta^{195}\text{Pt})$ . The data for the following complexes were taken from the literature:  $[(\eta^4\text{-C}_4\text{Me}_4)\text{PtCp}]^+$  [15];  $(\eta^4\text{-C}_4\text{H}_4)\text{RhCp}$  and  $(\text{cod})\text{Rh}(\text{acac})$  [16];  $\text{cis-}[\text{PtCl}_2(\text{CO})_2]$  [17] and  $\text{cis-}[\text{RhCl}_2(\text{CO})_2]^-$  [18];  $\{[\text{P}]\text{PtCl}\}^+$  [6]. The data for  $[\text{P}]\text{RhCp}$ ,  $[(\text{cod})\text{Pt}(\text{OC}(\text{Me})\text{CHC}(\text{Ph})\text{O})]^+$ ,  $\{[\text{P}]\text{PtCl}\}^+$  and  $[\text{P}]\text{RhCl}$  were determined in the present study.

NMR signals should appear at much lower frequencies [10].

Further evidence for the proposed structure stems from the  $^{195}\text{Pt}$  NMR spectrum [12] of **3** which is a doublet at  $\delta^{195}\text{Pt} -432.6$ . A roughly linear correlation between  $\delta^{195}\text{Pt}$  and  $\delta^{103}\text{Rh}$  data [13] (some of which were determined in this work) of comparable Pt(II) and Rh(I) complexes is depicted in Figure 3. The fact that the pair of data for **3** and **6** fits into this relationship indicates that both the molecular and electronic structures of the cationic platinum complex **3** and its neutral rhodium analogue **6** must be comparable.

## Experimental Section

### General and physical methods

All reactions were carried out under argon atmosphere in carefully dried solvents. The starting materials  $[\text{P}]\text{MCl}_2$  [ $\text{M} = \text{Pt}$  (**1**),  $\text{Pd}$  (**2**)] were prepared according to the published procedure [5].  $\text{AgPF}_6$  was used as commercial product without further purification.

NMR: Bruker ARX 250, Bruker DRX 500; chemical shifts are given with respect to  $\text{Me}_4\text{Si}$  ( $\delta^1\text{H}$  (acetone- $d_6$ ) = 2.04;  $\delta^{13}\text{C}$  (acetone- $d_6$ ) = 29.8;  $\delta^{31}\text{P} = 0$  for ext.  $\text{H}_3\text{PO}_4$ , 85% aq. with  $\Xi(^{31}\text{P}) = 40.480747$  MHz;  $\delta^{103}\text{Rh} = 0$  for  $\Xi(^{103}\text{Rh}) = 3.16$  MHz;  $\delta^{195}\text{Pt} = 0$  for  $\Xi(^{195}\text{Pt}) = 21.4$  MHz). Chemical shifts  $\delta^{103}\text{Rh}$  ( $\pm 1$  ppm) were determined by selective, heteronuclear  $^{31}\text{P}\{^{103}\text{Rh}, ^1\text{H}\}$  triple resonance experiments, using a special 5 mm probehead, tuneable to the frequencies of low- $\gamma$  nuclei, to  $^{31}\text{P}$  and  $^1\text{H}$ . EI-MS: Finnigan MAT 8500 (ionisation energy 70 eV); the  $m/e$  data refer to the isotopes  $^1\text{H}$ ,  $^{12}\text{C}$ ,  $^{31}\text{P}$ ,  $^{106}\text{Pd}$  and  $^{195}\text{Pt}$ . Decomposition points were determined using a Bchi 510 melting point apparatus.

### Synthesis of $\{[\text{MCl}[\text{P}(\eta^2\text{-C}_7\text{H}_7)_3]\}\text{PF}_6$ ( $\text{M} = \text{Pt}$ **3**, $\text{M} = \text{Pd}$ **4**)

At  $-78$  °C, solid  $\text{AgPF}_6$  (66 mg, 0.26 mmol) was added in one portion to the respective suspension containing  $[\text{P}]\text{MCl}_2$  ( $\text{M} = \text{Pt}$  **1**,  $\text{M} = \text{Pd}$  **2**) (0.20 mmol) in acetone (20 ml). The colour of the reaction mixture changed immediately to yellow (**1**) or violet (**2**). The suspensions were brought to room temperature under continuous stirring. The solvent was removed in a vacuum, the residues were dissolved again in acetone (50 ml), and insoluble material was filtered off. The volume of the filtrates was reduced to 5 ml, and ether (30 ml)

was added to give a yellow or violet precipitation which was separated and dried in a high vacuum.

{PtCl[P( $\eta^2$ -C<sub>7</sub>H<sub>7</sub>)<sub>3</sub>]PF<sub>6</sub> (3): yellow powder, m.p. 184 °C, yield 113 mg (88%). C<sub>21</sub>H<sub>21</sub>ClPPt<sup>+</sup>, EI-MS: *m/e* (%) = 534 (2) [M<sup>+</sup>], 408 (1) [P(C<sub>7</sub>H<sub>7</sub>)<sub>2</sub>Pt<sup>+</sup>], 350 (3) [P(C<sub>7</sub>H<sub>7</sub>)PtCl<sup>+</sup>], 304 (2) [P(C<sub>7</sub>H<sub>7</sub>)<sub>3</sub><sup>+</sup>], 91 (100) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>].

{PdCl[P( $\eta^2$ -C<sub>7</sub>H<sub>7</sub>)<sub>3</sub>]PF<sub>6</sub> (4): violet powder, m.p. 167 °C, yield 66 mg (74%). C<sub>21</sub>H<sub>21</sub>ClPPd<sup>+</sup>, EI-MS:

*m/e* (%) = 445 (3) [M<sup>+</sup>], 354 (9) [P(C<sub>7</sub>H<sub>7</sub>)<sub>2</sub>PdCl<sup>+</sup>], 304 (1) [P(C<sub>7</sub>H<sub>7</sub>)<sub>3</sub><sup>+</sup>], 91 (100) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>].

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- [1] a) R. B. King, R. N. Kapoor, M. S. Saran, P. N. Kapoor, *Inorg. Chem.* **10**, 1851 (1971); b) P. Braggeller, *Inorg. Chem.* **26**, 4125 (1987); c) P. Braggeller, *Inorg. Chim. Acta* **129**, L27 (1987); d) A. Handler, P. Peringer, E. P. Moller, *J. Organomet. Chem.* **412**, 451 (1991); e) W. Schuh, H. Kopacka, K. Wurst, P. Peringer, *Eur. J. Inorg. Chem.* **2001**, 2399.
- [2] S. Aizawa, T. Iida, S. Funahashi, *Inorg. Chem.* **35**, 5163 (1996).
- [3] M. Herberhold, K. Bauer, W. Milius, *Z. Anorg. Allg. Chem.* **620**, 2108 (1994).
- [4] M. Herberhold, K. Bauer, W. Milius, *J. Organomet. Chem.* **502**, C1 (1995).
- [5] M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, *Z. Anorg. Allg. Chem.* (2002) in press.
- [6] M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, *Inorg. Chim. Acta* (2002), in press.
- [7] M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, *Z. Naturforsch. Teil B*, (2002), in press.
- [8] M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, *Z. Anorg. Allg. Chem.* (2002), in press.
- [9] M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* **641**, 173 (2002).
- [10] M. Herberhold, W. Milius, S. Eibl, *Z. Anorg. Allg. Chem.* **625**, 341 (1999).
- [11] a) M. J. van Eis, H. Zappey, F. J. J. de Kanter, W. H. de Wolf, K. Lammertsma, F. Bickelhaupt, *J. Am. Chem. Soc.* **122**, 3386 (2000); b) M. J. van Eis, C. M. D. Komen, F. J. J. de Kanter, W. H. de Wolf, K. Lammertsma, F. Bickelhaupt, M. Lutz, A. L. Spek, *Angew. Chem.* **110**, 1656 (1998); *Angew. Chem. Int. Ed. Engl.* **37**, 1547 (1998).
- [12] For a review on <sup>195</sup>Pt NMR see: P. S. Pregosin, *Coord. Chem. Rev.* **44**, 247 (1982).
- [13] For a review on <sup>103</sup>Rh NMR see: B. E. Mann, in P. S. Pregosin (ed.): *Transition Metal Nuclear Magnetic Resonance*, pp. 177–215, Elsevier, Amsterdam (1991).
- [14] A. Bax, R. Freeman, *J. Magn. Reson.* **45**, 177 (1981).
- [15] G. E. Herberich, U. Englert, F. Marken, *J. Chem. Soc., Dalton Trans.* **1993**, 1979.
- [16] E. Maurer, S. Rieker, M. Schollbach, A. Schwenk, T. Egolf, W. von Philipsborn, *Helv. Chim. Acta* **65**, 26 (1982).
- [17] D. B. Dell'Amico, F. Calderazzo, C. A. Veracini, N. Zandonà, *Inorg. Chem.* **23**, 3030 (1984).
- [18] C. Brown, B. T. Heaton, L. Longhetti, W. T. Povey, D. O. Smith, *J. Organomet. Chem.* **192**, 93 (1980).