96. The Protonation of $[Pt_3(\mu\text{-CO})_3(PCy_3)_3]$

by **Klaus-Hermann Dahmen***, **Daniel Imhof**, and **Luigi M. Venanzi**

Laboratorium für Anorganische Chemie, ETH-Zentrum, Universitätstrasse 6, CH-8092 Zürich

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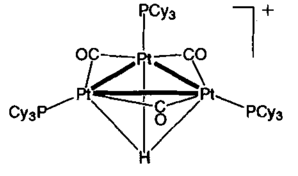
The cluster $[Pt_3(\mu\text{-CO})_3(PCy_3)_3]$ can be protonated with $HBF_4 \cdot OEt_2$ to form the cluster $[Pt_3(\mu\text{-CO})_3(PCy_3)_3(\mu_3\text{-H})]^+BF_4^-$ (**2**). This unstable compound was isolated and characterised by NMR and IR spectroscopy.

Introduction. – Clusters of the type $[Pt_3(\mu\text{-CO})_3(PR_3)_3]$ are good building blocks for the synthesis of heterometallic cluster compounds. Thus, this 42-e^- cluster can add *Lewis* acids such as M = Cu^+ [1], Ag^+ [2], and Au^+ [3], and ML = $Cu(PR_3)^+$ [1], $Ag(PR_3)^+$ [1], $Au(PR_3)^+$ [4], CuBr [5], and AgBr [5] without changing the structure of the Pt_3 unit to form either the 94-e^- sandwich $[\{Pt_3(\mu\text{-CO})_3(PR_3)_3\}_2M]^+$ or the 54-e^- halfsandwich $[\{Pt_3(\mu\text{-CO})_3(PR_3)_3\}(ML)]^+$ cluster.

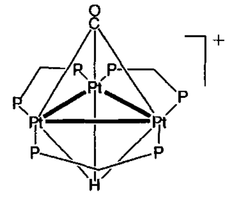
The metal centers of the above-mentioned heterometallic clusters are all isoelectronic, namely d^{10} centers. Furthermore, the fragments $Cu(PR_3)^+$, $Ag(PR_3)^+$, $Au(PR_3)^+$, CuBr, and AgBr are all isolobal [6–8], and thus, their LUMO orbitals have similar symmetry. They all have empty valence hybrid orbitals which can interact with the a_1-type MO orbital (HOMO) [9] of the $[Pt_3(\mu\text{-CO})_3(PR_3)_3]$ cluster.

The empty valence hybrid orbital of the fragment $Au(PR_3)^+$ has led to the suggestion that it can behave like H^+ [7] [10] [11]. The isolobal substitution of $Au(PR_3)^+$ for H^+ is now well established, as shown in the literature [4] [12–15] by the similarity of the structures of $[Os_3H_2(CO)_{10}]$ [16] and $[OsH\{Au(PPh_3)\}(CO)_{10}]$ [17].

Puddephatt and coworkers have very recently demonstrated that it is possible to substitute a coordinated H^+ by $Au(PR_3)^+$, in the cluster $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3(\mu_3\text{-H})]^+$ (dppm = $Ph_2PCH_2PPh_2$) [12]. Furthermore, *Mingos* and coworkers published in 1984 the structure of $[Pt_3(\mu\text{-CO})_3(PCy_3)_3\{\mu_3\text{-Au}(PR_3)\}]^+$ (Cy = cyclohexyl) [4]. *Braunstein* could show that the triangular cluster $[Pt_3(\mu\text{-CO})_3(PPh_3)_4]$ is converted to the edgebrigded tetrahedral cluster $[Pt_5(\mu\text{-CO})_6(PPh_3)_4]$ upon reaction with protons [18].



$[Pt_3(\mu\text{-CO})_3(PCy_3)_3(\mu_3\text{-H})]^+$



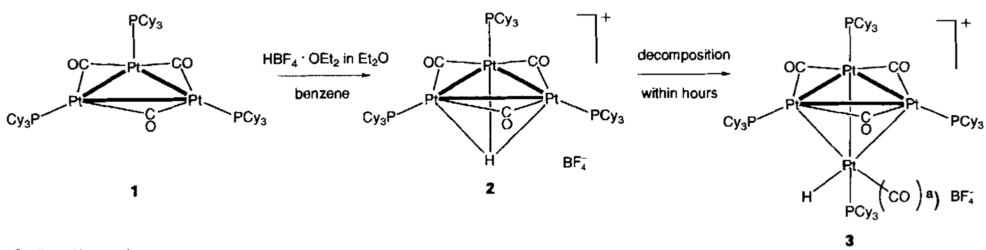
$[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3(\mu_3\text{-H})]^+$

We report here for the first time the protonation of the cluster $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ (**1**) by HBF_4 and the characterisation of the very air- and thermally sensitive product of the proposed structure $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3(\mu_3\text{-}H)]BF_4$ (**2**) by ^{1}H- and ^{31}P-NMR and IR spectroscopy. This cationic cluster **2** is analogous to the known cluster $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3(\mu_3\text{-}H)]^+$ of *Lloyd* and *Puddephatt* [19].

Results and Discussion. – A series of experiments to protonate the 42-e^- cluster $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ (**1**) simply by adding an acid to the solution of **1** failed, because of immediate decomposition of the cluster to afford many unidentified products.

The reaction of $HBF_4 \cdot OEt_2$ with **1** in solvents such as MeOH or CH_2Cl_2 led to spontaneous decomposition. However, in the more basic solvent THF, no reaction was observed. Finally, protonation of **1** was successfully achieved by addition of $HBF_4 \cdot OEt_2$ to a benzene solution of **1**, leading to the immediate precipitation of the brown cationic cluster $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3(\mu_3\text{-}H)]^+$ as the tetrafluoroborate salt **2** (*Scheme*). This air-sensitive compound is not very stable, even after isolation and storage in an inert atmosphere.

Scheme



a) See discussion.

However, careful experimentation allowed its complete characterisation. All NMR spectra were recorded with the precipitated solid **2** redissolved in CD_2Cl_2. The coordination of the proton to the Pt cluster can be clearly seen in its ^{1}H-NMR spectrum (*Fig. 1*).

The chemical shift of the proton of **2** at −8 ppm lies within the typical hydride region. The hydron couples equally to the ^{195}Pt and ^{31}P atoms. The observed pattern of resonances is determined mainly by the three ^{195}Pt isotopomers as sketched in *Fig. 2*. The main *q* in the spectrum arises mainly from the isotopomer **I** (*M* part of A_3M-spin system). The resonances of *M* spin of the isotopomers **II** and **III** show a first-order spectrum because of the equivalence of the M spin with respect to all other coupling partners and because of the clear and large separation of the lines due to the large value of the $^1J(^{195}Pt,^1H)$ coupling constant. Therefore, the spin system of isotopomer **II**, a $A_2A'MX$, can be considered as an A_3MX spin system which gives rise to *dq* in the spectrum.

The $^{31}P\{^1H\}$-NMR spectrum of **2** (see *Fig. 3b*) is very similar to that of the unprotonated cluster **1** [20] [21]. A homodecoupled ^{31}P-NMR spectrum shows (*Fig. 3a*) the main signal (a *s*) of isotopomer **I** as a *d*, indicating that there is only one hydron capping symmetrically the $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ unit. The $^{31}P\{^1H\}$- and the ^{1}H-NMR data are given in *Table 1*.

The NMR spectra were all measured at room temperature even though fast decomposition occurred during the measurement. At low temperature, all signals were slightly

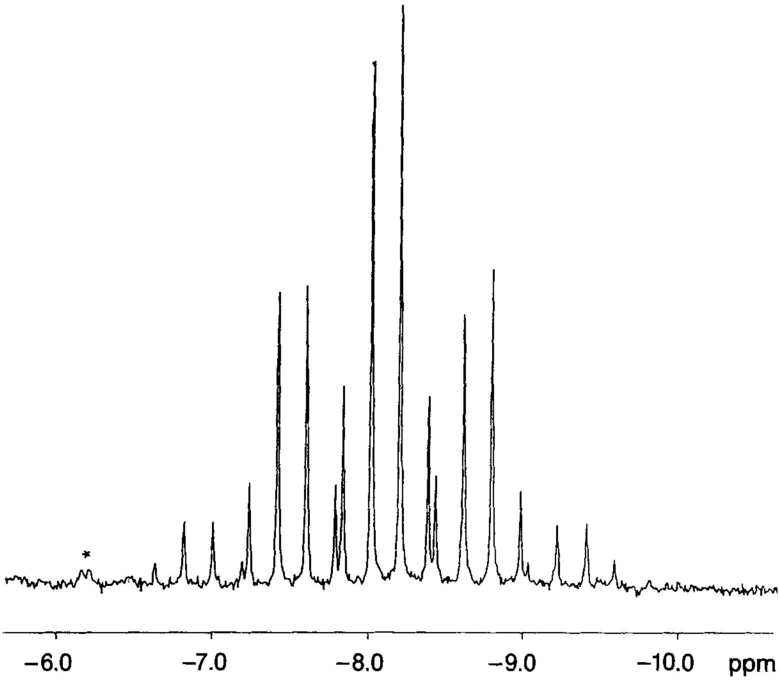


Fig. 1. *Hydride region of ^1H-NMR spectrum of* **2** *in CD_2Cl_2 at 22°.* The resonances marked with an asterix are due to decomposition products.

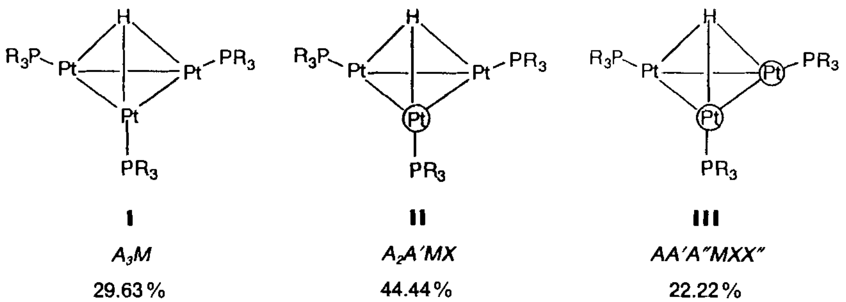
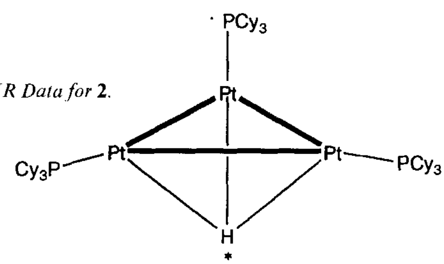


Fig. 2. *The most abundant isotopomers of* **2**. The NMR-active Pt-atom is circled.

Table 1. *^1H- and $^{31}P\{^1H\}$-NMR Data for* **2**. δ in ppm and J in Hz.

Atom X	δ	^1J(Pt,X)	^2J(Pt,X)	^2J(P,X)	^3J(P,X)
P	38.0	5360	204	–	11
H*	–8.0	292	–	46	–



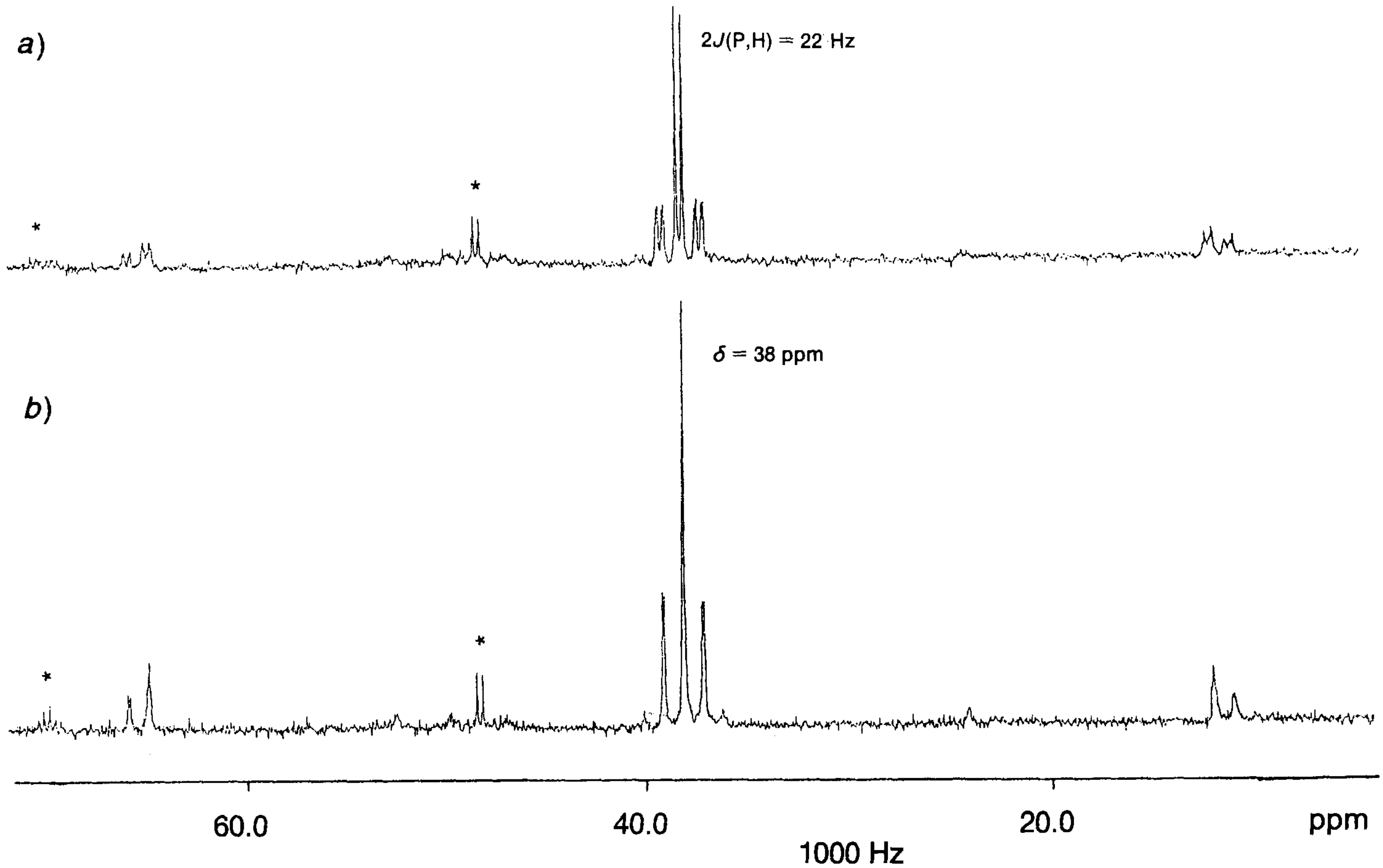


Fig. 3. *^{31}P-NMR Spectrum of* **2** *in CD_2Cl_2 at 22°*: a) *homo-decoupled and* b) *proton-decoupled spectrum.* The resonances marked with an asterix are due to decomposition products.

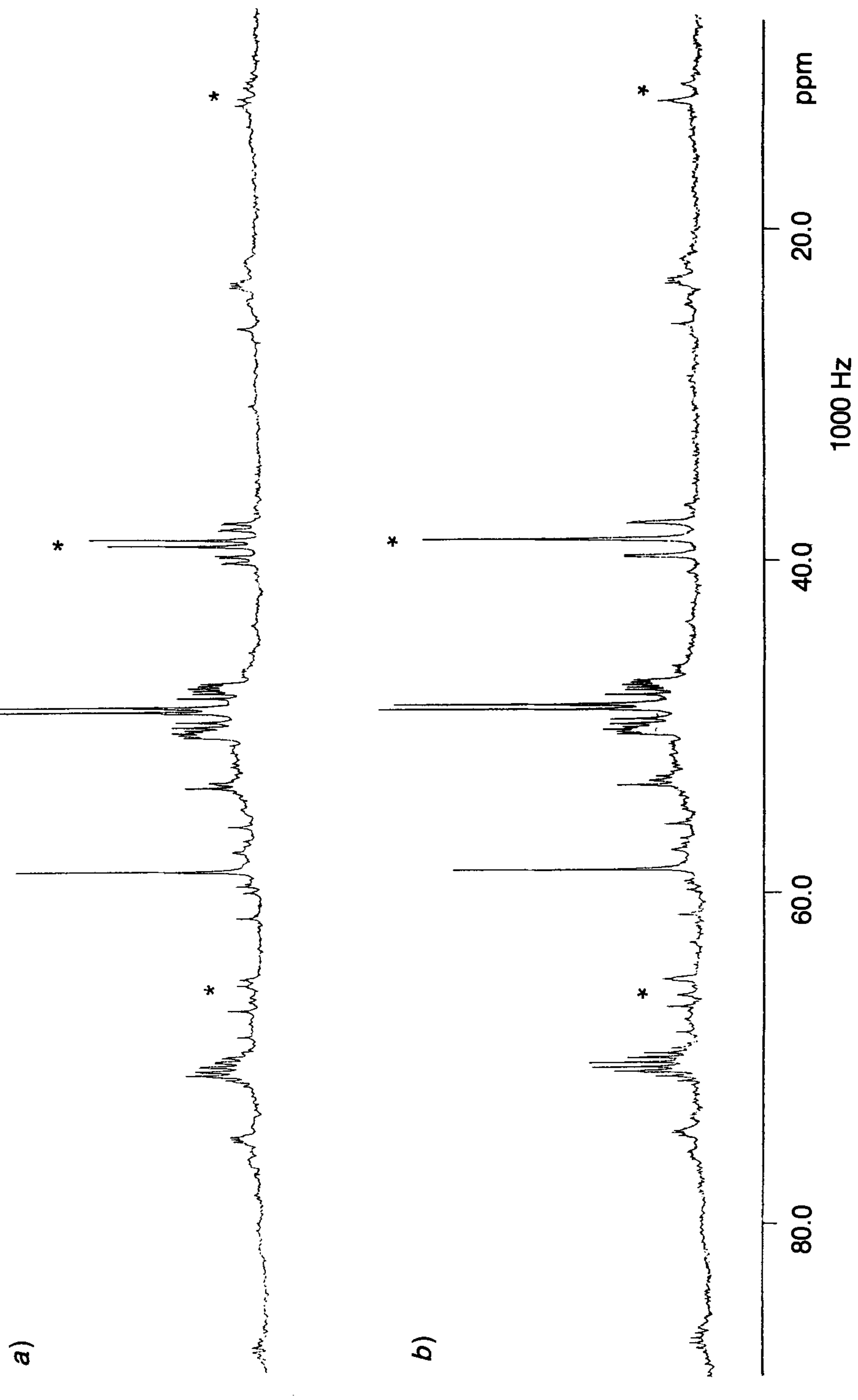


Fig. 4. *^{31}P-NMR Spectrum of* **3** *in CD_2Cl_2 at 22°:* a) *homo-decoupled and* b) *proton-decoupled spectrum.* The resonances marked with an asterix are due to product **2**.

broadened, possibly indicating either an inter- or intramolecular dynamic behaviour. Beside this broadening of the signals, which is also observable for the unprotonated Pt_3 cluster, no significant change of the pattern was observed in the $^{31}P\{^1H\}$-NMR spectrum not even at −70°.

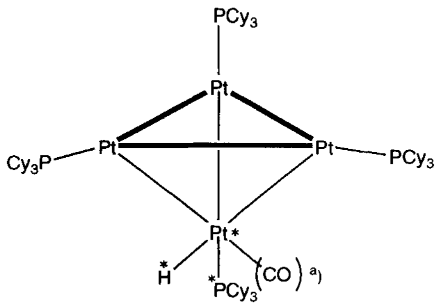
The protonated cluster **2** decomposed in the solid state within hours, and thus its characterisation was not easily accomplished. The IR spectrum shows a medium broad $\tilde{\nu}$ (Pt−H) at 2020 cm^{-1} and strong $\tilde{\nu}$(CO) frequencies in the region 1800 cm^{-1}. All attempts to grow crystals by changing solvents, even at −30°, failed. Also a change of the phosphine ligands in $[Pt_3(\mu\text{-}CO)_3L_3]$ to L = $P(i\text{-}Pr)_3$, $PPh(i\text{-}Pr)_2$ did not help to stabilise the corresponding compound.

The decomposition can be followed by $^{31}P\{^1H\}$-NMR spectroscopy. One of the decomposition products can be identified as a new cluster **3** composed of the basic unit $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ and a capped $[\mu_3\text{-}PtH(PCy_3)]^+$ fragment (*Scheme*). In the $^{31}P\{^1H\}$-NMR spectrum, two different P-resonances (*Fig. 4*) can be observed. The pattern at 49 ppm is a typical $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ pattern with further couplings of a Pt*−P* unit. The additional P* coupling leads to a *d* splitting of the main signal (a part of spin system A_3M of the isotopomer without ^{195}Pt). The M part of this spin system can be clearly observed at 71 ppm with a *q* (further signals are due to the superposition of the other isotopomers). The Pt*, symmetrically capping the Pt_3 triangle, can be clearly identified by the isotopomer where this Pt* is NMR-active thus leading to a A_3MY spin system. While the A part (49 ppm) shows a *dd*, with ^2J(Pt*,P) = 208 and ^3J(P*,P) = 32 Hz, the M part at 71 ppm gives rise to a *dq* (broad) which corresponds to the ^1J(Pt*,P*) coupling constant of 3388 Hz. A partially decoupled ^{31}P-NMR spectrum leads only to a further splitting of the M-part, thus indicating that a hydride is coordinated onto the Pt*−P* unit.

Indeed, the ^1H-NMR spectrum of **3** shows in the hydride region a six-line resonance at −5.2 ppm, from where the coupling constants ^1J(Pt*,H*) and ^2J(Pt,H*) can be determined. Further splitting of this six-line system are due to the ^{195}Pt isotopes of the cluster unit. The ^{31}P- and ^1H-NMR data are given in *Table 2*.

Table 2. *^1H- and $^{31}P\{^1H\}$-NMR Data for* **3**. δ in ppm and J in Hz.

Atom X	δ	^1J(Pt,X)	^2J(Pt,X)	^1J(Pt*,X)	^2J(Pt*,X)	^2J(P*,X)	^3J(P*,X)
P	49.0	5213	280	–	208	–	32
P*	71.3	–	113	3388	–	–	–
H*	−5.3	–	100	341	–	10	–



a) See discussion.

It is possible that the attached $[Pt(H)(PCy_3)]^+$ unit bears a CO ligand. However, compound **3** is not sufficiently stable to allow its separation and isolation and decomposes further to many unidentified products. From solution IR spectra of this reaction mixture, it is not clear if the carbonyl frequency in the typical region of 2000 cm^{-1} stems from **3** or from other decomposition products.

The electron count leads to 54-e^- which is the typical value found for half-sandwich clusters. However, the $[Pt(H)(PCy_3)(CO)]^+$ unit is isolobal to the $Au(PR_3)^+$ or H^+ fragment and, therefore, a possible candidate for an addition product.

Attempts to stabilise this Pt_3 cluster by the incorporation of a different $[Pt(L)(PR_3)(CO)]^+$ fragment have so far failed; however, we hope that we will be successful in the near future.

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Experimental Part

General. All chemicals were obtained from *Fluka*. The cluster $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ was prepared as described elsewhere [22]. All manipulations were carried out under Ar by using *Schlenk* techniques. IR Spectra: *Perkin Elmer1430*; nujol mulls; $\tilde{\nu}_{max}$ in cm^{-1}. NMR Spectra: *Bruker-WM-250* and *-HX-90* instruments; δ in ppm, J in Hz. Elemental C and H analysis were carried out by the Microanalytical Service of the Organic Chemistry Laboratory of ETH-Zürich. The heavy elements and their ratios were determined by the Analytical Service of the Inorganic Chemistry Laboratory of the ETH Zürich using either atomic absorption or X-ray fluorescence spectroscopy (XFS).

Tri-μ-carbonyl-μ₃-hydro-tris [tri(cyclohexyl)phosphine]triplantinum (3 Pt–Pt*) Tetrafluoroborate* (*$[Pt_3(\mu\text{-}CO)_3(PCy_3)_3(\mu_3\text{-}H)]BF_4$*; **2**). $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ (100 mg, 0.066 mmol) was dissolved in benzene (3 ml) and the soln. saturated with Ar by passing Ar through the soln. Then 54% HBF_4/Et_2O soln. (12 mmol) was added. After a short time of mixing, the mixture was centrifuged and the solvent removed from a brown precipitate. The residue was washed twice with cold hexane. The product was dried under high vacuum: 87 mg (82%) of **2**. IR: 1830v*s* (CO), 1810*s*, 1799*s*. 2060 *m* (br., H). $^{31}P\{^1H\}$-NMR (101 MHz, CD_2Cl_2): δ 38; $^1J(Pt,P) = 5360$,. $^2J(Pt,P) = 204$, $^3J(P,P) = 11$, $^2J(P,H) = 46$ (off resonance). ^1H-NMR (90 MHz, CD_2Cl_2): δ −8; $^1J(Pt,H) = 292$, $^2J(P,H) = 46$. Calc. for $C_{57}H_{100}O_3P_3Pt_3BF_4$: C 42.8, H 6.30; found: C 41.2, H 6.34. XFS calc.: P36.6%, P/Pt = 1.00; found: Pt 36.4 ± 00.3%, P/Pt = 1.03 ± 0.04.

REFERENCES

[1] K.-H. Dahmen, Ph.D. Thesis, ETH-Zürich, No. 8172, 1986.
[2] A. Albinati, K.-H. Dahmen, A. Togni, L.M. Venanzi, *Angew. Chem. Int. Ed.* **1985,** *24,* 766.
[3] M.F. Hallam, D.M.P. Mingos, T. Adatia, M. McPartin, *J. Chem. Soc., Dalton Trans.* **1987,** 335.
[4] C.E. Briant, R.W.M. Wardle, D.M.P. Mingos, *J. Organomet. Chem.* **1984,** *267,* C49.
[5] A. Stockhammer, K.-H. Dahmen, T. Gerfin, V. Gramlich, W. Petter, L.M. Venanzi, *Helv. Chim. Acta* **1991,** *74,* 989.
[6] M. Elian, M.M.L. Chen, D.M.P. Mingos, R. Hofmann, *Inorg. Chem.* **1976,** *15,* 1148.
[7] R. Hoffmann, *Angew. Chem. Int. Ed.* **1982,** *21,* 711.
[8] F.G.A. Stone, *Angew. Chem.* **1984,** *96,* 85.
[9] D.J. Underwood, R. Hoffmann, K. Tatsumi, A. Nakamura, Y. Yamamoto, *J. Am. Chem. Soc.* **1985,** *107,* 5968.
[10] P. Braunstein, J. Rose, *Gold Bull.* **1985,** *18,* 17.
[11] R. Hoffmann, *Angew. Chem. Int. Ed.* **1982,** *21,* 711.
[12] N.C. Payne, R. Ramachandran, G. Schoettel, J.J. Vittal, R.J. Puddephatt, *Inorg. Chem.* **1991,** *30,* 4048.

[13] T. M. G. Carneiro, D. Matt, P. Braunstein, *Coord. Chem. Rev.* **1989,** *96,* 49.
[14] B. Colbran, C. M. Hay, B. F. G. Johnson, F. Lahoz, J. Lewis, P. R. Raithby, *J. Chem. Soc., Dalton Trans.* **1986,** 1766.
[15] A. Albinati, F. Demartini, P. Janser, L. F. Rhodes, L. M. Venanzi, *J. Am. Chem. Soc.* **1989,** *111,* 2115.
[16] A. Orpen, E. Bryan, D. Pippard, G. Sheldrick, *J. Chem. Soc., Chem. Commun.* **1979,** 723.
[17] F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithlay, *J. Organomet. Chem.* **1981,** *215,* C33.
[18] P. Braunstein, 'Perspectives in Coordination Chemistry,' Eds. A. F. Williams, C. Floriani, and A. E. Merbach, VCH, New York, 1992, p. 67–107.
[19] B. R. Loyd, R. J. Puddephatt, *J. Am. Chem. Soc.* **1985,** *107,* 7785.
[20] A. Moor, P. S. Pregosin, L. M. Venanzi, *Helv. Chim. Acta* **1981,** *48,* 153.
[21] A. Moor, Ph. D. Thesis, ETH-Zürich, No. 7176, 1982.
[22] K.-H. Dahmen, A. Moor, R. Naegeli, L. M. Venanzi, *Inorg. Chem.* **1991,** *30,* 4286.