# Synthesis, Solid-State Structure and Multinuclear NMR Studies of the New Polyhydrido Iridium Carbonyl Cluster $Ir_4H_4(\mu\text{-}H)_4(CO)_4(PPh_3)_4$

**Luigi Garlaschelli,*[a] Francesco Greco,[a] Giulia Peli,[a] Mario Manassero,*[b] Mirella Sansoni,[b] Roberto Gobetto,*[c] Luca Salassa,[c] and Roberto Della Pergola[d]**

**Keywords:** Cluster compounds / Iridium / Hydride ligands / NMR spectroscopy / P ligands

The carbonyl hydride cluster $Ir_4H_8(CO)_4(PPh_3)_4$ (**1**) has been formed in high yield and purity by heating a mixture of $Ir_4(CO)_{12}$ and $PPh_3$ in toluene at 90 °C under hydrogen at atmospheric pressure. The product has been characterised by microanalysis, spectroscopy (IR, $^1H$ and $^{31}P$ NMR) and X-ray diffraction. In the solid state one hydrogen, one CO and one triphenylphosphane ligand are terminally bonded to each iridium atom, whereas four hydride ligands are bridging. All the hydrogen atoms were directly located by X-ray analysis at an average H–Ir distance of 1.55 Å (for the terminal H) and 1.75 Å (for the μ-H). As shown by $^1H$ and $^{31}P$ NMR spectra, two isomeric forms (**1A** and **1B**) of the cluster are present in $CD_2Cl_2$ solution at room temperature, and they do not interconvert in the explored temperature range. However, if a solid sample of the cluster is dissolved at 188 K, only **1A** is detected by NMR spectroscopy. The structure of **1B** could be proposed on the basis of the $T_1$ relaxation times of the various hydrides: it results by localised exchange of H and CO around two vertices of the tetrahedral frame.

Hydrogen atoms are common ligands in transition metal chemistry[1] and can be bound to the cluster framework in a variety of ways.[2] Beside the most common terminal, bridging, and face-capping modes,[3] they can also occupy an interestitial coordination mode site, with up to six H-metal interactions.[4,5]

The hydride ligands in many clusters are abstracted from the solvent in which the cluster is prepared.[6] However, hydrides can also be introduced using a rational synthetic route, commonly acidification of an anionic cluster,[5,7,8] or hydrogenation of a suitable precursor.[9] Alternatively, the precursor might have contained hydrides and these are carried over into the cluster product.[10]

Owing to their low scattering factors, hydride ligands are difficult to locate by X-ray crystallography, and frequently neutron diffraction studies must be undertaken.[4,11,12] NMR spectroscopy is a powerful tool for determining the position of the hydrides in solution (especially when the cluster contains other nuclei with spin 1/2, such as $^{31}P$, $^{103}Rh$ or $^{195}Pt$).[13] A few cases of solid-state $^1H$ NMR studies have also been reported.[14]

In the present work we report the spectroscopic characterisation and the solid-state structure of the new cluster $[Ir_4H_8(CO)_4(PPh_3)_4]$, which can be obtained in a one-pot synthesis directly from $Ir_4(CO)_{12}$, $PPh_3$ and hydrogen. Among the huge number of tetrahedrally substituted iridium clusters,[12,15–17] the compound described here is peculiar in several aspects: the simplicity of the synthesis, the highly symmetric structure, its straightforward dynamic behaviour, and the large number of ligands around a small tetrahedral core. As one half of the ligands are hydrides, the compound can model the dissociative chemisorption of hydrogen on small iridium particles.[18]

$[H_2Ir_4(CO)_{10}]^{2-}$, with two terminal hydrides,[15] and $[HIr_4(CO)_{11}]^-$, with a bridging hydride located from neutron diffraction,[12] are other examples of hydrido-carbonyl clusters of iridium; $[HIr_4(CO)_{10}PPh_3]^-$ [19] and $[HIr_4(CO)_{10}PPh_2]$,[20] are tetranuclear clusters containing both hydride and P-donor ligands.

---

[a] Dipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Università di Milano,
Via G. Venezian 21, 20133 Milano, Italy
Fax: (internat.) + 39-02/5031-4405
E-mail: luigi.garlaschelli@unimi.it
[b] Dipartimento di Chimica Strutturale e Stereochimica Inorganica dell'Università di Milano,
Via G. Venezian 21, 20133 Milano, Italy
E-mail: m.manassero@istm.cnr.it
[c] Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali dell'Università di Torino,
Via P. Giura 7, 10125 Torino, Italy
E-mail: roberto.gobetto@ch.unito.it
[d] Dipartimento di Scienze dell'Ambiente e del Territorio dell'Università degli Studi di Milano Bicocca,
Piazza della Scienza 1, 20126 Milano, Italy

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

DOI: 10.1002/ejic.200200690

## Results

### Synthesis and Chemical Characterisation

While trying to synthesise an iridium cluster containing an interestitial phosphido atom, $Ir_4(CO)_8(PPh_3)_4$ [17] (**2**) was heated in refluxing toluene under a hydrogen atmosphere. The infrared spectrum of the brownish-yellow solution suggested the formation of a mixture. Attempts to separate the main products by preparative TLC or column chromatography failed, and therefore we sought milder conditions in order to increase the selectivity of the reaction. Eventually, a two-step, one-pot synthesis was devised, which is more simple and more selective: the first step is the carbonyl substitution of $Ir_4(CO)_{12}$ accomplished in refluxing toluene, with $PPh_3$ and $Ir_4(CO)_{12}$ in a 4:1 molar ratio. In the second step, the mixture of partially substituted clusters is placed under hydrogen and heated gently at a temperature below 90 °C until the infrared spectrum shows complete conversion (usually 24 hours). The product was crystallised from $CH_2Cl_2$/cyclohexane and was formulated as $Ir_4H_8(CO)_4(PPh_3)_4$ (**1**), by means of microanalysis, NMR spectroscopy, and X-ray analysis.

The poor reactivity of **1** is evidence of its stability. Despite the large number of hydride ligands, **1** cannot be deprotonated by base: when it was dissolved in THF, with an excess of $Na_2CO_3$ or KOH, the IR spectrum did not show any modification. A toluene solution of $Ir_4H_8(CO)_4(PPh_3)_4$ was placed under a carbon monoxide atmosphere at room temperature and no reaction was detected after three hours. However, heating the same solution at 110 °C for four hours resulted in the transformation into a mixture of $Ir_4(CO)_9(PPh_3)_3$ and **2**.

### Solid-State Structure

The solid-state structure of **1**, and the numbering scheme, are shown in Figure 1. Relevant distances and angles are collected in Table 1. The metallic framework is tetrahedral, but the (idealised) molecular symmetry is $S_4$, with the unique axis intersecting the two unbridged Ir−Ir bonds. Thus, the four equivalent iridium vertices are coordinated by one triphenylphosphane, one terminal CO, one terminal and two bridging hydride ligands. The cluster is only slightly distorted by the presence of four μ-H ligands: the unbridged edges measure 2.726 Å and the bridged ones 2.919 Å. The five ligands are arranged in a square-based pyramidal coordination, with the $PPh_3$ ligands in the axial positions. The P-donors are almost perfectly mutually *trans*, separated by an unbridged Ir−Ir bond, and *cis* to the bridging hydride (with corresponding P−Ir−Ir angles of 115°) and therefore the metal atoms are octahedrally surrounded. The average distances between metals and ligands of different nature are well within the normal range for iridium clusters,[12,16,19,20] and are collected in Table 1. The Ir−H bond lengths are obviously affected by high standard deviations (0.03−0.04 Å) and therefore differences of 0.1 Å are of little significance; however, constant trends for the Ir−(μ-H)−Ir bond lengths seem to suggest some asymmetry, with long bonds *trans* to the carbonyl and short bonds *trans* to the terminal hydride, a pattern contrasting with the "structural" trans effect in octahedral metal complexes, being smaller for CO than for H.[21]

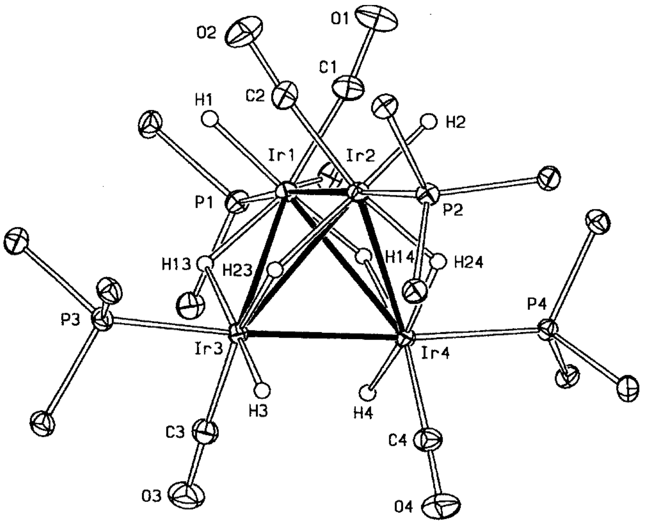


Figure 1. The solid state structure of **1**; for clarity, only the *ipso* carbon atoms of the phenyl rings are indicated; ellipsoids are drawn at 30% probability

Table 1. Selected distances (Å) and angles (deg.) in $[Ir_4H_8(CO)_4(PPh_3)_4]$ (**1**) with estimated standard deviations (esd's) on the last figure in parentheses; term = terminal; br = edge bridging; tr = *trans*

| | | | |
|---|---|---|---|
| Ir1−Ir2 | 2.721(1) | Ir1−C1 | 1.846(3) |
| Ir1−Ir3 | 2.925(1) | Ir2−C2 | 1.847(3) |
| Ir1−Ir4 | 2.916(1) | Ir3−C3 | 1.854(3) |
| Ir2−Ir3 | 2.906(1) | Ir4−C4 | 1.855(3) |
| Ir2−Ir4 | 2.931(1) | | |
| Ir3−Ir4 | 2.732(1) | Ir1−P1 | 2.305(1) |
| Ir1−H1 | 1.62(4) | Ir2−P2 | 2.315(1) |
| Ir2−H2 | 1.58(3) | Ir3−P3 | 2.315(1) |
| Ir3−H3 | 1.51(4) | Ir4−P4 | 2.320(1) |
| Ir4−H4 | 1.51(4) | | |
| Ir1−H13 | 1.71(3) | Ir3−H13 | 1.80(3) |
| Ir1−H14 | 1.60(4) | Ir3−H23 | 1.69(4) |
| Ir2−H23 | 1.82(3) | Ir4−H14 | 1.87(4) |
| Ir2−H24 | 1.63(4) | Ir4−H24 | 1.86(3) |
| Average distances | | Average angles | |
| C−O | 1.143 | $P-Ir-H_{br}$ | 88 |
| Ir−P | 2.314 | $H_{br}-Ir-H_{br}$ | 102 |
| Ir − CO | 1.850 | $H_{term}-Ir-CO$ | 86 |
| $Ir\text{-}H_{term}$ | 1.55 | $H_{term}-Ir-P$ | 89 |
| $Ir-H_{br}$ | 1.75 | P−Ir−CO | 96 |
| | | $P-Ir-Ir_{tr}$ | 175 |
| | | $P-Ir-Ir_{cis}$ | 115 |
| | | Ir−C−O | 174 |

### Multinuclear VT NMR Spectroscopy

When a sample of **1** is dissolved at low temperature in $CD_2Cl_2$ the $^1H$ NMR spectrum shows only two absorptions in the hydride region, at $\delta = -15.24$ and $-17.25$ ppm respectively, in agreement with the presence of the terminal and bridging hydride ligands of the highly symmetric structure determined by X-ray analysis. As the temperature is increased three new resonances appear in the proton spectrum at $\delta = -14.82$, $-16.11$ and $-18.89$ ppm, respectively, in the relative ratio 2:1:1. The intensity of these new absorptions is temperature dependent, as shown in Figure 2.

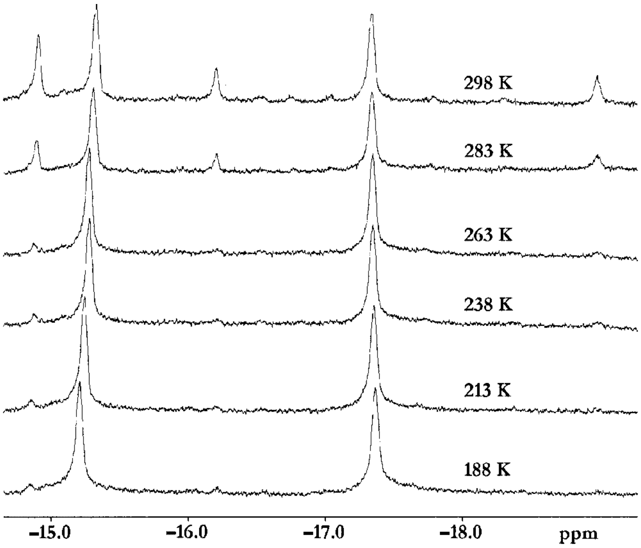
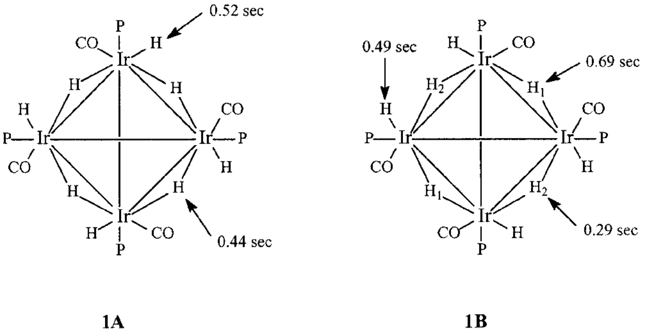


Figure 2. The $^1H$ NMR spectrum of **1**, recorded in $CD_2Cl_2$, at variable temperature

The high-field resonance can readily be assigned to a terminal hydride, whereas the two lower field signals are consistent with the formation of two distinct bridging hydride absorptions.

The same process has also been examined by $^{31}P$ and $^{13}C$ NMR spectroscopy. Monitoring the VT $^{31}P$ NMR spectrum in the same range of temperature, one can easily see that at 188 K only one $^{31}P$ signal is present at $\delta = 3.5$ ppm, whereas upon increasing the temperature a second absorption is observed at $\delta = 4.2$ ppm; at room temperature the spectrum shows two signals. Similarly, only a single resonance is detected in the $^{13}C$ NMR spectrum for the sample dissolved at 188 K in $CD_2Cl_2$, whereas a second absorption can be observed in the carbonyl region when the temperature is increased ($\delta = 166.78$ and 165.80 ppm).[22] Obviously the new resonances in the $^1H$, $^{13}C$, and $^{31}P$ NMR spectra must be associated with the formation of a second isomer (**1B**; Scheme 1), different from that found in the solid state (**1A**), which increases in concentration at higher temperature. The two resonances in the $^{31}P$ NMR spectrum were unambiguously assigned to **1A** ($\delta = 3.5$ ppm) and **1B** ($\delta = 4.2$ ppm) by running a $^1H$-$^{31}P$ 2D experiment. It is worth noting that if the sample is recrystallised again and a new experiment is performed with the previously reported procedure the same results are obtained. However, if the solution containing **1A** and **1B** at equilibrium is cooled to 188 K, both isomers are present; thus, the rate of exchange between the two isomers is slow on the NMR timescale.



Scheme 1. The structure of isomers **1A** and **1B**, with the $T_1$ relaxation times of the different hydride ligands

On the basis of the spectroscopic results it is reasonable to suggest that the second structure is also highly symmetric and the difference with respect to the former one is due to the position of the hydride ligands on the metal framework.

In order to assign the structure of the isomer **1B** an evaluation of the longitudinal relaxation times ($T_1$) of the hydride resonances has been performed. It has previously been demonstrated that this technique provides a suitable method for the determination of the structures of polyhydridic cluster systems[23] due to the dependence of $T_1$ on the relative interproton distances.[24]

The $T_1$ values obtained for the hydride ligands of the two isomers at room temperature are reported in Scheme 1, and are proposed on the basis of the relaxation and symmetry data.

The difference between the two isomers is the reciprocal orientation of CO and terminal H around the tetrahedron: by inverting the position of these ligands at two iridium vertices the molecular symmetry is lowered from $S_4$ to $D_2$. The $T_1$ values of the terminal hydrides are similar in both isomers, whereas the bridging hydrides show substantial changes. In particular, the relaxation time for the higher-field signal of **1B** is substantially shorter than the others, indicating a closer proximity of these hydrides to other hydride ligands in the cluster. On this basis it is straightforward to assign the resonance at $\delta = -18.89$ ppm (having shorter $T_1$) to the $H_2$ hydride in the structure. All the other attributions are summarised in Figure 3.

The complex spin system of twelve $^{31}P$ and $^1H$ nuclei, further complicated by chemical exchange, could not be examined in details. As a matter of fact, the observed bands are so broadened (either by chemical exchange or by low resolution at 188 K) that no hyperfine structure was observed at all (expected values for $^2J_{P,H} = 5-10$ Hz).[19,20]

## Experimental Section

**General:** All the solvents were purified and dried by conventional methods and stored under nitrogen. All the reactions were carried out under an oxygen-free nitrogen atmosphere using standard Schlenk-tube techniques.[25] $Ir_4(CO)_{12}$ was prepared by literature methods.[26]

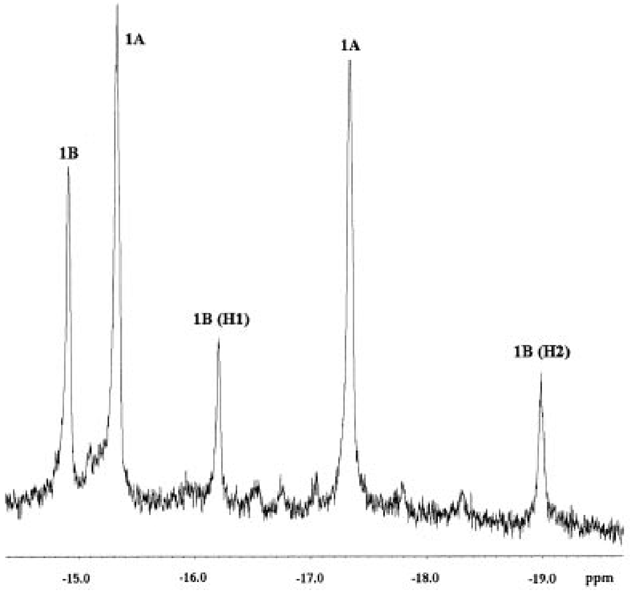


Figure 3. The $^1H$ NMR spectrum of **1**, recorded in $CD_2Cl_2$, at room temperature, with the assignments of the peaks

NMR experiments were performed on a JEOL EX 400 spectrometer ($^1H$ operating frequency 399.78 MHz); non-selective inversion recovery was used to obtain $^1H$ $T_1$ values. Samples for $T_1$ measurements were prepared in the absence of $O_2$ by using standard freeze-pump-thaw techniques. Temperature calibration was carried out with a standard methanol $^1H$ thermometer. Errors in the reported $T_1$ values were estimated to be in the range ±2%.

**Synthesis of $Ir_4H_8(CO)_4(PPh_3)_4$:** $Ir_4(CO)_{12}$ (0.55 g, 0.50 mmol) and $PPh_3$ (0.52 g, 2 mmol) were suspended in 40 mL of toluene. The mixture was refluxed for 7 hours, and the IR spectrum of the yellow solution showed bands consistent with a mixture of tri- and tetra-substituted derivatives of $Ir_4(CO)_{12}$. The inert atmosphere was removed and the Schlenk was refilled with hydrogen. The solution was heated at 80 °C for about 24 hours and the colour changed from the yellow to pale yellow. After cooling, the solution was filtered, and the solvent was removed in vacuo. The residue was dissolved in dichloromethane and layered with cyclohexane. Yellow prismatic crystals were obtained in 65% yield (0.63 g). IR: ν(CO): 2121w 1993s $cm^{-1}$ in $CH_2Cl_2$. $C_{76}H_{68}Ir_4O_4P_4$ (1938.1): calcd. C 47.1, H 3.5 found C 47.2, H 3.6.

**X-ray Data Collection and Structure Determination:** Crystal data are summarised in Table 2; other experimental details are listed in the supporting information. The diffraction experiment was carried out on a Bruker SMART CCD area-detector diffractometer at 223 K. No crystal decay was observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT,[27] and an absorption correction was applied (SADABS)[28] to the collected reflections. The calculations were performed using the Personal Structure Determination Package[29] and the physical constants tabulated therein.[30] The structure was solved by direct methods (SHELXS)[31] and refined by full-matrix least-squares using all reflections and minimising the function $\Sigma w(F_o^2 - kF_c^2)^2$ (refinement on $F^2$). Anisotropic thermal factors were refined for all the non-hydrogen atoms. The eight hydridic hydrogen atoms were refined with isotropic thermal factors. The remaining hydrogen atoms were placed in their ideal positions (C−H = 0.97 Å), with the thermal parameter $B$ 1.10-times that of the carbon atom to which they are attached and not refined. In the final difference Fourier map the maximum residual was 1.88(81) e·Å$^{-3}$ at 0.81 Å from Ir(2). CCDC-199711 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or at Cambridge crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystallographic data

| | |
|---|---|
| Formula | $C_{76}H_{68}Ir_4O_4P_4$ |
| $M$ | 1938.08 |
| Colour | pale yellow |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ (no.14) |
| $a$/Å | 15.196(1) |
| $b$/Å | 24.237(2) |
| $c$/Å | 18.949(2) |
| α/° | 90 |
| β/° | 106.13(1) |
| γ/° | 90 |
| $V$/Å$^3$ | 6704.3(9) |
| $Z$ | 4 |
| $F$(000) | 3696 |
| $D_c$/g cm$^{-3}$ | 1.92 |
| $T$/K | 223 |
| Crystal dimensions (mm) | 0.29 × 0.41 × 0.58 |
| μ (Mo-$K_\alpha$)/cm$^{-1}$ | 80.28 |
| Min. and max. transm. factors | 0.50−1.00 |
| Scan mode | ω |
| Frame width/° | 0.30 |
| Time per frame/sec | 10 |
| No. of frames | 3650 |
| Detector-sample distance/cm | 4.00 |
| θ-range/° | 3−26 |
| Reciprocal space explored | full sphere |
| No. of reflections (total; independent) | 164038; 20468 |
| $R_{int}$ | 0.039 |
| Final $R_2$ and $R_{2w}$ indices[a] ($F^2$, all reflections) | 0.034, 0.060 |
| Conventional $R_1$ index [$I > 2\sigma(I)$] | 0.022 |
| Reflections with $I > 2\sigma(I)$ | 17033 |
| No. of variables | 825 |
| Goodness of fit[b] | 1.00 |

[a] $R_2 = [\Sigma(|F_o^2 - kF_c^2|/\Sigma F_o^2]$, $R_{2w} = [\Sigma w(F_o^2 - kF_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [b] $[\Sigma w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (0.04F_o^2)^2]^{1/2}$, $N_o$ is the number of observations and $N_v$ the number of variables.

**Supporting Information:** The $^{13}C$ NMR spectra for this article are available (see footnote on the first page of this article).

## Acknowledgments

This work was funded by MIUR.

---

[1] *Recent Advances in Hydride Chemistry* (Eds.: M. Peruzzini and R. Poli), Elsevier, Amsterdam (The Netherlands) **2001**.

[2] A. P. Humpries, H. D. Kaesz, *Prog. Inorg. Chem.* **1979**, *25*, 145−222.

[3] A. Albinati, L. M. Venanzi, *Coord. Chem. Rev.* **2000**, *200−202*, 687−715.

[4] R. Bau, M. H. Drabnis, L. Garlaschelli, W. T. Klooster, Z. Xie, T. F. Koetzle, S. Martinengo, *Science* **1997**, *275*, 1099−1102.

[5] D. W. Hart, R. G. Teller, C.-Y. Wei, R. Bau, G. Longoni, S. Campanella, P. Chini, T. F Koetzle, *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 80−81.

[6] [6a] A. J. Amoroso, B. F. G. Johnson, J. Lewis, P. R. Raithby, W. T. Wong, *J. Chem. Soc., Chem. Commun.* **1991**, 814−815. [6b] P. J. Bailey, M. A. Beswick, B. F. G. Johnson, J. Lewis, M. McPartlin, P. R. Raithby, M. C. Ramirez de Arellano, *J. Chem. Soc., Dalton Trans.* **1996**, 3515−3520.

[7] [7a] M. Manassero, M. Sansoni, G. Longoni, *J. Chem. Soc., Chem. Commun.* **1976**, 919−920. [7b] R. Della Pergola, C. Bandini, F. Demartin, E. Diana, L. Garlaschelli, P. L. Stanghellini, P. Zanello, *J. Chem. Soc., Dalton Trans.* **1996**, 747−754.

[8] A. Ceriotti, R. Della Pergola, L. Garlaschelli, F. Laschi, M. Manassero, N. Masciocchi, M. Sansoni, P. Zanello, *Inorg. Chem.* **1991**, *30*, 3349−3357.

[9] [9a] S. A. R. Knox, J. W. Koepke, M. A. Andrews, H. D. Kaesz, *J. Am. Chem. Soc.* **1975**, *97*, 3942−3952. [9b] L. M. Bavaro, P. Montangero, J. B. Keister, *J. Am. Chem. Soc.* **1983**, *105*, 4977−4981.

[10] [10a] R. Della Pergola, L. Garlaschelli, F. Demartin, M. Manassero, N. Masciocchi, G. Longoni, *J. Organomet. Chem.* **1988**, *352*, C59−C62. [10b] G. Ciani, M. Moret, A. Sironi, P. Antognazza, T. Beringhelli, G. D'Alfonso, R. Della Pergola, A. Minoja, *J. Chem. Soc., Chem. Commun.* **1991**, 1255−1257. [10c] C. S. Yang, C. P. Cheng, *J. Chem. Soc., Dalton Trans.* **1994**, 2011−2014.

[11] A. Bashall, L. H. Gade, J. Lewis, B. F. G. Johnson, G. J. McIntyre, M. McPartlin, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1164−1166.

[12] R. Bau, M. Chiang, C.-Y. Wei, L. Garlaschelli, S. Martinengo, T. F. Koetzle, *Inorg. Chem.* **1984**, *23*, 4758−4762.

[13] [13a] S. Martinengo, B. T. Heaton, R. J. Goodfellow, P. Chini, *J. Chem. Soc., Chem. Commun.* **1977**, *2*, 39−40. [13b] T. Beringhelli, A. Ceriotti, G. D'Alfonso, R. Della Pergola, G. Ciani, M. Moret, A. Sironi, *Organometallics* **1990**, *9*, 1053−1059. [13c] M. J. Davis, R. Roulet, *Inorg. Chim. Acta* **1992**, *197*, 15−20.

[14] [14a] S. Aime, P. J. Barrie, D. F. Brougham, R. Gobetto, G. E. Hawkes, *Inorg. Chem.* **1995**, *34*, 3557−3559. [14b] T. Eguchi, B. T. Heaton, R. Harding, K. Miyagi, G. Longoni, J. Nahring, N. Nakamura, H. Nakayama, T. A. Pakkanen, J. Pursiainen, A. K. Smith, *J. Chem. Soc., Dalton Trans.* **1996**, 625−630. [14c] T. Eguchi, B. T. Heaton, *J. Chem. Soc., Dalton Trans.* **1999**, 3523−3530.

[15] G. Ciani, M. Martinengo, V. G. Albano, F. Canziani, G. Giordano, S. Martinengo, P. Chini, *J. Organomet. Chem.* **1978**, *150*, C17−C19.

[16] [16a] G. F. Stuntz, J. R. Shapley, *J. Organomet. Chem.* **1981**, *213*, 389−403. [16b] D. C. Sonnenberger, J. D. Atwood, *Organometallics* **1982**, *1*, 694−698. [16c] D. Braga, R. Ros, R. Roulet, *J. Organomet. Chem.* **1985**, *286*, C8−C12. [16d] R. Della Pergola, L. Garlaschelli, S. Martinengo, F. Demartin, M. Manassero, M. Sansoni, *Gazz. Chim. Ital.* **1987**, *117*, 245−247. [16e] B. E. Mann, B. T. Pickup, A. K. Smith, *J. Chem. Soc., Dalton Trans.* **1989**, 889−893. [16f] M. P. Brown, D. Burns, M. M. Harding, S. Maginn, A. K. Smith, *Inorg. Chim. Acta* **1989**, *162*, 287−289. [16g] F. Ragaini, F. Porta, F. Demartin, *Organometallics* **1991**, *10*, 185−189. [16h] A. Strawczynski, C. Hall, G. Bondietti, R. Ros, R. Roulet, *Helv. Chim. Acta* **1994**, *77*, 754−770. [16i] R. Della Pergola, L. Garlaschelli, S. Martinengo, M. Manassero, M. Sansoni, *J. Organomet. Chem.* **2000**, *593−594*, 63−68.

[17] D. C. Sonnenberger, J. D. Atwood, *Inorg. Chem.* **1981**, *20*, 3243−3246.

[18] A. M. Argo, J. F. Odzak, F. S. Lai, B. C. Gates, *Nature* **2002**, *415*, 623−626.

[19] R. Della Pergola, L. Garlaschelli, M. Manassero, M. Sansoni, D. Strumolo, *J. Cluster Sci.* **2001**, *12*, 23−34.

[20] F. S. Livotto, P. R. Raithby, M. D. Vargas, *J. Chem. Soc., Dalton Trans.* **1993**, 1797−1803.

[21] B. J. Coe, S. J. Glenwright, *Coord. Chem. Rev.* **2000**, *203*, 5−80.

[22] See Figure 4s in the supporting information.

[23] S. Aime, W. Dastrù, R. Gobetto, A. Viale, in *Recent Advances in Hydride Chemistry*, ref.[1]

[24] [24a] A. Abragham, *The Principles of Nuclear Magnetic Resonance*, Oxford University Press, **1961**. [24b] A. E. Derome, *Modern NMR Techniques for Chemistry Research*, **1987**, Pergamon, Oxford. [24c] D. W. Claridge, *High-Resolution NMR Techniques in Organic Chemistry*, Tetrahedron Organic Chemistry Series Volume 19, **1999**, Pergamon, Oxford.

[25] D. F. Shriver; M. A. Dredzon, *The Manipulation of air-sensitive compounds*, 2nd ed. **1986**, Wiley New York.

[26] R. Della Pergola, L. Garlaschelli, S. Martinengo, *Inorg. Synth.* **1991**, *28*, 245−247.

[27] SAINT Reference manual, Siemens Energy and Automation, Madison, WI, **1994−1996**.

[28] G. M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Gottingen, 1997.

[29] B. A. Frenz, *Comput. Phys.* **1988**, *2*, 42.

[30] *Crystallographic Computing 5*, Oxford University Press: Oxford, U. K., **1991**; Chapter 11, p. 126.

[31] G. M. Sheldrick, (**1985**). SHELXS 86. Program for the solution of crystal structures. Univ. of Gottingen, Germany.

Received December 17, 2002