ELSEVIER

Journal of Organometallic Chemistry 492 (1995) 35–39

Journal of Organometallic Chemistry

Heterobimetallic indenyl complexes. Synthesis and structure of *syn*-[Cr(CO)$_3$($\mu,\eta:\eta$-indenyl)Rh(COD)] [☆]

Chiara Bonifaci [a], Alberto Ceccon [a,*], Alessandro Gambaro [a], Paolo Ganis [a,1], Saverio Santi [a], Giovanni Valle [b], Alfonso Venzo [c]

[a] *Dipartimento di Chimica Fisica, Università di Padova, Via Loredan 2, 35131 Padova, Italy*
[b] *C.N.R., Centro di Studio sui Biopolimeri, Via Marzolo 3, 35131 Padova, Italy*
[c] *C.N.R., Centro di Studio sugli Stati Molecolari, Radicalici ed Eccitati, via Loredan 2, 35131 Padova, Italy*

Received 13 July 1994

Abstract

The heterobimetallic complex *syn*-[Cr(CO)$_3$($\mu,\eta:\eta$-indenyl)Rh(COD)] was obtained by reaction of *syn*-[Cr(CO)$_3$($\mu,\eta:\eta$-indenyl)Rh(CO)$_2$] with COD. The stereochemistry was retained in the exchange reaction as confirmed by ^{1}H and ^{13}C NMR measurements and by X-ray diffractometric analysis. In spite of great distortion, the COD complex is quite stable. An unusual bonding interaction between the hybrid C≡O orbitals of the Cr(CO)$_3$ group and the s-orbital of methine hydrogen atoms of COD is inferred on the basis of spectroscopic and X-ray structural data.

Keywords: Chromium; Rhodium; Indenyl; *Syn* and *anti* structures; X-ray structure

1. Introduction

Complexes in which two metal atoms are connected by an organic bridge are known. In principle, with an aromatic or a cyclic polyolefin as a bridge, the two metal atoms can be located either on the same side (*syn*-facial variant) or on opposite sides (*anti*-facial variant) of the ligand plane [1–5].

Systems in which the bridge is a fused two-ring aromatic compound have not been widely explored, the only examples reported so far being the bimetallic *anti* complexes of naphthalene [6] and pentalene [7]. We and others have prepared and described some *anti*-hetero- [8] and *anti*-homo-bimetallic [9] indenyl complexes which exhibit appreciable slip–fold distortion of metal bonding with the aromatic rings. To our knowledge, no examples of *syn*-bimetallic complexes with a bicyclic bridging ligand have been reported so far, except those recently synthesized in our laboratory [2]. We have been able to prepare the *anti*- [8c,d] and *syn*- [11] isomers of the complex [Cr(CO)$_3$($\mu,\eta:\eta$-indenyl)Rh(CO)$_2$] and have found that the formation of the *anti*- or *syn*-species is controlled by the nature of the ancillary ligands at rhodium.

The *anti*-coordination of the benzene ring of the (η-indenyl)Rh(COD) moiety with the Cr(CO)$_3$ group does not modify significantly the geometry of the Rh–cyclopentadienyl ring sub-unit [8b] even though the reactivity at rhodium is greatly increased [8d,12]. Conversely, when the Cr(CO)$_3$ and RhL$_2$ groups are bonded to indenyl in a *syn*-configuration, the rhodium appears to be far less reactive [12] and the structure is strongly modified [11]. In particular, in the case of the *syn*-isomer of [Cr(CO)$_3$($\mu,\eta:\eta$-indenyl)Rh(NBD)] (**3**) we observed large deviations of the indenyl frame from planarity, highly distorted coordination of norbornadiene to rhodium and unusually short distances between the CO groups and some NBD hydrogen atoms. De-

---

[☆] Work supported, in part, by the C.N.R. (Rome) through its Progetto Finalizzato Chimica Fine II.

[*] Corresponding author.

[1] On sabbatical leave from University of Napoli, Italy.

[2] A particular case of a *syn*-homobimetallic complex is represented by [V$_2$(indenyl)$_2$] reported by Jonas et al. [10].

SSDI 0022-328X(94)05280-8

spite these molecular constraints, the complex is quite stable, which was attributed to a Cr–Rh interaction.

In this paper, we discuss the effect of the substitution of COD for NBD. The great stability found for this *syn*-isomer of [Cr(CO)$_3$(μ,μ:η-indenyl)Rh(COD)] is explained on the basis of X-ray structural analysis and NMR spectroscopic evidence.

2. Results and discussion

An air-stable orange-brown powder was obtained by treating (40°C, 7 h) a methylene chloride solution of *syn*-[Cr(CO)$_3$-(μ,η:η-indenyl)Rh(CO)$_2$], *syn*-(**2**), with a large excess of COD. The product was identified as *syn*-[Cr(CO)$_3$(μ,η:η-indenyl)Rh(COD)], *syn*-(**1**). When compared to the *anti*-isomer, the ^{1}H NMR spectrum of *syn*-(**1**) (see Experimental details) shows a downfield shift ($\Delta\delta$ 0.49 ppm) of the H$_2$ signal and large upfield shifts ($\Delta\delta$ -1.09 and -1.43 ppm) for the resonances of H$_{1,3}$ and H$_{4,7}$, respectively. In the ^{13}C NMR spectrum, the most striking differences observed in comparison to *anti*-(**1**) are the upfield shift of the C$_{1,3}$, C$_2$, C$_{4,7}$ and C≡O signals ($\Delta\delta$ -13.22, -14.96, -9.17 and -1.20 ppm, respectively), and the downfield shift of the C$_{3a,7a}$ resonances ($\Delta\delta$ $+22.26$ ppm). These differences are quite similar to those observed in a comparison of the proton and carbon chemical shifts of the *anti*- [8d] and *syn*- [11] stereoisomers of [Cr(CO)$_3$(μ,η:η-indenyl)Rh(CO)$_2$] and confirm that the *syn*-arrangement of the metals is not changed in the ligand-exchange reaction. The resonances due to the four olefinic protons of COD appear as a broad signal at δ 4.17 ppm, and those of the methylene protons are observed at δ 2.48 (broad peak, 4H) and δ 2.08 (multiplet, 4H) ppm, respectively. As the temperature is lowered, the COD signals broaden further, collapse (at 280 K those at δ 2.48 ppm, at 266 K those at δ 4.17 ppm and at 262 K those at δ 2.08 ppm) and finally re-emerge as two multiplets for each initial resonance (δ 2.74 and 2.22, 4.22 and 4.06, and 2.12 and 2.01 ppm, respectively, at 212 K). For this fluxional process, a mean value of $\Delta G^{\ddagger} = 53.9 \pm 0.8$ kJ mol^{-1} was calculated.

Crystals of *syn*-(**1**) suitable for diffractometric analysis were obtained from methylene chloride solutions. A view of the molecular structure giving the atom number scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 1.

A *hinge* angle (ca. 13°) of the plane [C(4), C(5), C(6), C(7)] with the plane [C(7), C(7a), C(1), C(3), C(3a), C(4)] and a *slippage* of the Cr(CO)$_3$ group towards the C(5)—C(6) bond of ca. 0.07 Å are observed. Thus the Cr bonding to the indenyl benzene moiety can be interpreted more reasonably as η^4 rather than distorted η^6. On the side of Rh(COD), there is a large *hinge* angle between the planes [C(1), C(2), C(3)] and [C(7), C(7a), C(1), C(3), C(3a), C(4)] (ca. 17°). These data are consistent with pronounced allylic character of the frame [C(1), C(2), C(3)], that is with increasing importance of η^3-coordination of the Rh(COD) group to the indenyl. This assumption is also supported by the bond lengths C(1)—C(2) 1.419(9) Å and C(2)—C(3) 1.413(7) Å as against C(1)—C(7a) 1.448(6) Å and C(3)—C(3a) 1.449(8) Å.

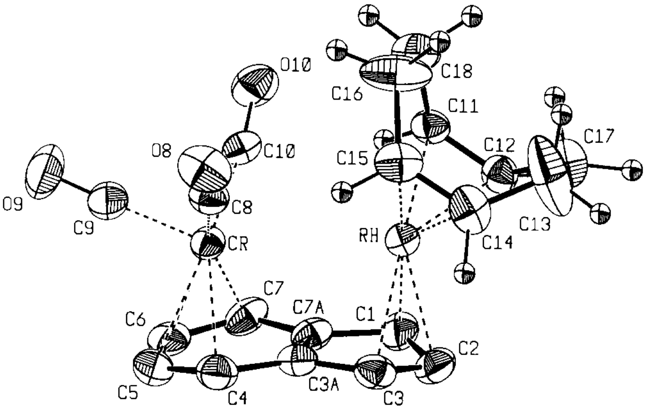

Fig. 1. A perspective view of the molecule of [Cr(CO)$_3$(μ,η:η-indenyl)Rh(COD)], *syn*-(**1**).

Table 1
Selected geometrical parameters for the complex *syn*-[Cr(CO)$_3$-(μ,η : η-indenyl)Rh(COD)], *syn*-(**1**)

Bond distances (Å)			
Rh–C(1)	2.213(5)	Rh–C(2)	2.165(7)
Rh–C(3)	2.260(6)	Rh–C(3a)	2.593(5)
Rh–C(7a)	2.565(5)	Rh–C(11)	2.142(6)
Rh–C(12)	2.124(5)	Rh–C(14)	2.140(5)
Rh–C(15)	2.171(5)	Cr–C(3a)	2.434(7)
Cr–C(4)	2.255(7)	Cr–C(5)	2.194(6)
Cr–C(6)	2.189(5)	Cr–C(7)	2.267(5)
Cr–C(7a)	2.464(6)	Cr–C(8)	1.844(5)
Cr–C(9)	1.820(7)	Cr–C(10)	1.855(6)
O(8)–C(8)	1.164(6)	O(9)–C(9)	1.153(9)
O(10)–C(10)	1.145(8)	C(1)–C(2)	1.419(9)
C(1)–C(7a)	1.448(6)	C(2)–C(3)	1.413(7)
C(3)–C(3a)	1.449(8)	C(3a)–C(4)	1.426(7)
C(3a)–C(7a)	1.426(7)	C(4)–C(5)	1.420(8)
C(5)–C(6)	1.420(9)	C(6)–C(7)	1.411(7)
C(7)–C(7a)	1.419(8)	C(11)–C(12)	1.393(9)
C(14)–C(15)			
C(8) · · · H(15)	2.39	O(8) · · · H(15)	2.33
C(10) · · · H(11)	2.40	O(10) · · · H(11)	2.33
O(8) · · · H(16)8	3.01	O(10) · · · H(18)	2.58
Bond angles (°)			
C(9)–Cr–C(10)	84.4(3)	Cr–C(8)–O(8)	172.5(5)
C(8)–Cr–C(10)	85.1(3)	Cr–C(9)–O(9)	178.1(7)
C(8)–Cr–C(10)	89.3(3)	Cr–C(10)–O(10)	173.3(5)
Torsion angles (°) [a]			
C(8)–Cr–P–C(3a)	32.5	C(11)–C(18)–C(16)–C(15)	3.5
C(9)–Cr–P–C(5)	36.0	C(14)–C(13)–C(17)–C(12)	9.4
C(10)–Cr–P–C(7)	24.0		

[a] P indicates the location of the centre of the benzene ring.

These findings are consistent with the NMR results which indicate that the same structural features persist in solution. The minor interaction of C(3a) and C(7a) in *syn*-(**1**) compared to *anti*-(**1**) is revealed by the small effect of $Cr(CO)_3$ on their chemical shift ($\Delta\delta$ −8.29 ppm), substantially less than that in *anti*-(**1**) ($\Delta\delta$ −26.12 ppm). Moreover, the tetrahedral tendency of the C(1, 3) and C(4, 7) carbon atoms, as suggested by the increased hinge angle on going from *anti*-(**1**) to *syn*-(**1**), is demonstrated by the large upfield shift experienced by the corresponding ^1H and the ^{13}C resonances. Finally, the importance in *syn*-(**1**) of η^3-bonding of the five-membered ring (and, consequently, of the allylic character of the C(1)—C(2)—C(3) frame) to rhodium is suggested by the higher chemical shift differences found for the hydrogen and carbon nuclei in positions 1 and 3 with respect to those in position 2 upon complexation with $Cr(CO)_3$, as discussed elsewhere [8c].

The C≡O groups facing the COD form angles Cr—C≡O (ca. 173°) and C—Cr—C (ca. 85°) which deviate considerably from ideal values to increase the interatom distances from COD. The coordination about Rh is strongly distorted, as shown by the large dihedral angle between the planes [C(11), C(12), C(14), C(15)] and [C(1), C(2), C(3)] (ca. 26°). For an undistorted geometry, they would be parallel [8c,d]. In *syn*-(**1**) the COD approaches the more unstable conformation characterized by a *pseudo* C_{2v} symmetry, resulting from almost eclipsing torsion angles about the bonds C(13)—C(17) and C(16)—C(18) (see Table 1). This is different from the *trans* isomer [8c] and its permethylated derivative [8e].

The most significant differences between the *syn* complexes **1**, **2** and **3** concern the metal–metal distances and the intramolecular interactions between the C≡O groups bonded to chromium and the ancillary ligands of rhodium. The Cr ··· Rh distance in **1** (3.27 Å) is larger than the 3.08 Å in **2** and the 3.18 Å in **3**. This parameter has been discussed in a previous comunication [11] and it has been interpreted as indicating a weak bond. To support this suggestion, the contribution of the two π-electrons of the C(3a) — C(7a) bond (elongated to ca. 1.46 Å) was invoked for **3**, probably forming a multicentre bond with Cr and Rh. In contrast, the C(3a) — C(7a) bond length in **1** is 1.426(7) Å which excludes any involvement of its π-electrons, except for problematic distorted η^6,η^5 hapticities to produce closed-shell configurations for the two metals. The longer Cr ··· Rh bond can only be very weak. The two metal atoms should have electronic configurations with a pronounced unsaturated character. One would therefore expect **1** to be less stable than its homologues **2** and **3**, but the stabilities of the three *cis* complexes are comparable.

One may pose the question of which structural features counterbalance the severe molecular distortions of **1**. As reported in the Experimental details, almost all the hydrogen atoms have been located from difference Fourier syntheses. A few seem to play an important role in the relative stability of the complex. In particular, the hydrogen atoms H(11) and H(15) lie almost exactly on the normal to the mid-points of the C(8)≡O(8) and C(10)≡O(10) bonds at distances of 2.27 Å and 2.30 Å, respectively. They are almost 0.40–0.45 Å shorter than the sums of the van der Waals radii. This would suggest a strong repulsive effect. Approximate calculations performed using Pauling's van der Waals radii [13] and Sheraga's formulae [14] indicate repulsive energies of ca. 5–6 kcal mol^{-1} which are underestimates. The observed bond lengths for **1** are to be interpreted as real bond distances, in which an overlap can be surmised between the hybrid C≡O orbitals and the s orbital of the hydrogen atom. This stabilizing interaction seems to be the only one capable of stabilizing the above-mentioned molecular constraints. The compound seems to develop this unusual interaction to compensate for the apparently unsaturated electronic configurations. This resembles an 'agostic' bond in some respects, although it is a metal–hydrogen interaction. Certainly it cannot be thought of as a hydrogen bond, due to the peculiar geometrical arrangement of the atoms involved. The methylene hydrogen atoms H(18) and H(16) also interact with O(10) and O(8) at distances of ca. 2.60 Å and 3.02 Å, respectively, but to a lesser extent and quite differently stereochemically.

The existence of the CO ··· H interaction is confirmed by the increased activation free energy of rotation around the indenyl–Rh bond ($\Delta G^{\ddagger} = 53.9$ kJ mol^{-1}) compared to that of *anti*-(**1**) ($\Delta G^{\ddagger} = 38.0$ kJ mol^{-1}) [8d]. The lower reactivity of the *syn*-species in the ligand exchange reactions can also be attributed to the CO ··· H interaction, even though large steric effects are expected to play a significant role.

3. Experimental details

The synthesis of *syn*-(**1**) was performed under purified argon, and oxygen-free solvents and reagents were used. The complex, *syn*-(**1**), was obtained in quantitative yield by reaction of *syn*-$[Cr(CO)_3(\mu,\eta:\eta$-indenyl$)Rh(CO)_2]$ (**2**) [11] in CH_2Cl_2 with a large excess of COD at 40°C for 7 h. Pumping off the solvents and COD gave an orange–brown residue which was crystallized from CH_2Cl_2/pentane. Instruments: mass spectrum, 70 eV EI, VG-16 MicroMass; IR: Perkin-Elmer 1600 FT-IR; NMR, Bruker AM-400 (^1H, 400.133 MHz; ^{13}C, 100.614 MHz). The ^1H and ^{13}C NMR spectra were recorded in CD_2Cl_2 solution at 298 K and the chemical shift values are given in ppm from internal Me_4Si.

IR spectra were run as CH_2Cl_2 solutions within CaF_2 windows. M.p. 137–139°C (decomp.). MS m/z: 462, M^+ (calc.: 462). IRν(C≡O) (cm^{-1}): 1942 (vs), 1867 (vs). ^1H NMR (solvent CD_2Cl_2, 25°C, assignments confirmed by {^{1}H}-^{1}H NOE) δ: 6.89 (m, 1H, $J(^{103}Rh\text{-}H) = 2.1$ Hz, H_2); 5.21, 4.59 (m, 2H each, AA′BB′, $H_{5,6}$ and $H_{4,7}$, respectively); 3.98 (m, 2H, $H_{1,3}$) ppm. COD resonances δ: 4.17 (m, 4H, olefinic protons); 2.48, 2.06 (m, 4H each, CH_2) ppm. {^{1}H}-^{13}C NMR (solvent CD_2Cl_2, 25°C, assignments made by selective ^{1}H decoupling) δ: 235.41 (Cr—C≡O); 109.78 (d, $J(^{103}Rh\text{-}C) < 0.4$ Hz, $C_{3a,7a}$); 89.23 (d,$J(^{103}Rh\text{-}C) = 6.3$ Hz, C_2); 88.91 ($C_{5,6}$); 76.80 ($C_{4,7}$); 61.97 (d,$J(^{103}Rh\text{-}C) = 5.3$ Hz, $C_{1,3}$) ppm. COD resonances δ: 73.23 (d,$J(^{103}Rh\text{-}C) = 12.0$ Hz, CH); 31.88 (CH_2) ppm.

3.1. *Collection of X-ray diffraction data. Determination and refinement of the structure.*

X-ray quality crystals of *syn*-(**1**) were grown from a saturated solution of CH_2Cl_2. Single crystals were mounted on a Philips PW-100 computer-controlled four-circle diffractometer with graphite monochromator. Standard centring and auto-indexing procedures indicated a centred monoclinic lattice, space group $C2/c$. The orientation matrix and accurate unit cell dimensions were determined from angular settings of 25 high-angle reflections. The intensities were corrected for Lorentz and polarization effects and for absorption by empirical methods (ψ-scan). Crystallographic data are consolidated in Table 2. The structure was solved by a Patterson synthesis and completed from difference maps. All non-hydrogen atoms were refined with anisotropic thermal parameters. Almost all the hydrogen atoms were located from difference Fourier syntheses (the remaining were geometrically determined), and they were included in the final calculations and refined in riding mode with $U(H) = 1.2U(C)_{eq}$. Blocked-cascade least-squares refinements were used. They converged to the final conventional R index of 0.040. An unitary weighting scheme was used. Scattering factors for the atoms were taken from Cromer and Waber [15]; the scattering factors for Cr and Rh were corrected for the real and imaginary parts of the anomalous dispersion using Cromer's values [16]. All computations were carried out on a Cyber 76 computer using the SHELX-76 program [17]. The final positional parameters of the non-hydrogen atoms are listed in Table 3. The anisotropic thermal parameters

Table 2
Summary of the crystal data and intensity data collection for the complex *syn*-[Cr(CO)$_3$-(μ,η:η-indenyl)Rh(COD)], *syn*-(**1**)

Formula	$C_{20}H_{19}CrO_3Rh$
M	462.27
Crystal dimensions (mm)	0.25×0.20×0.30
T(K)	298
Radiation	graphite monochromated Mo Kα (λ = 0.7107)
Space group	$C2/c$
a (Å)	18.671(8)
b (Å)	15.262(6)
c (Å)	13.859(5)
β (°)	119.0(1)
V (Å^3)	3454.06
Z	8
D_c (g cm^{-1})	1.78
F(000)	1856
μ (cm^{-1})	16.83
Scan speed (deg mm^{-1})	2.0 in the 2θ scan mode
Scan width (deg)	1.2
Take off angle (deg)	3
2θ range	$3.0 < 2\theta < 45$
Total reflections	4165
Reflections used for refinement [a]	2643
Solution method	Patterson
Hydrogen atoms detected	15
Refined parameters	282
R [b] (on F_o)	0.040
R_w [c]	0.043
Goodness of fit [d]	0.706
Highest map residuals (e Å^{-3})	0.90

[a] $F_0^2 \geq 2\sigma(F_0^2)$.
[b] $R = \Sigma \| F_0 | - | F_c \| / \Sigma | F_0 |$.
[c] $R_w = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w F_0^2]^{1/2}$.
[d] G.O.F. $= [\Sigma w(|F_0| - |F_c|)^2 / (N_0 - N_b)^2]^{1/2}$.

Table 3
Fractional coordinates with equivalent isotropic thermal parameters (Å^2) for *syn*-[Cr(CO)$_3$(μ,η:η-indenyl)Rh(COD)], *syn*-(**1**)

Atom	x	y	z	U_{eq} [a]
Rh	0.25125(2)	0.37261(2)	0.18932(3)	0.0313(2)
Cr	0.36159(5)	0.37331(4)	0.45810(6)	0.0337(3)
O(8)	0.3257(2)	0.5662(2)	0.4309(3)	0.061(2)
O(9)	0.3942(3)	0.3969(4)	0.6889(3)	0.085(2)
O(10)	0.1943(2)	0.3320(3)	0.4249(3)	0.058(2)
C(1)	0.3145(3)	0.2458(3)	0.2097(4)	0.042(2)
C(2)	0.3310(3)	0.3035(3)	0.1425(4)	0.047(2)
C(3)	0.3789(3)	0.3745(3)	0.2077(4)	0.044(2)
C(3a)	0.4074(3)	0.3513(3)	0.3221(4)	0.037(2)
C(4)	0.4667(3)	0.3900(3)	0.4228(5)	0.047(2)
C(5)	0.4917(3)	0.3427(4)	0.5224(4)	0.051(2)
C(6)	0.4496(3)	0.2653(3)	0.5229(5)	0.050(2)
C(7)	0.3831(3)	0.2329(3)	0.4251(4)	0.043(2)
C(7a)	0.3666(3)	0.2717(3)	0.3233(4)	0.037(2)
C(8)	0.3347(3)	0.4906(3)	0.4415(4)	0.044(2)
C(9)	0.3828(4)	0.3884(4)	0.5998(5)	0.054(3)
C(10)	0.2565(3)	0.3469(3)	0.4310(4)	0.041(2)
C(11)	0.1343(3)	0.3421(3)	0.1744(4)	0.039(2)
C(12)	0.1349(3)	0.3196(3)	0.0774(4)	0.041(2)
C(13)	0.1263(5)	0.4581(6)	−0.0248(6)	0.112(4)
C(14)	0.2040(3)	0.4816(3)	0.0788(4)	0.050(2)
C(15)	0.2052(3)	0.5051(3)	0.1770(4)	0.046(2)
C(16)	0.1308(4)	0.5076(4)	0.1904(7)	0.076(4)
C(17)	0.0938(4)	0.3709(4)	−0.0295(5)	0.058(3)
C(18)	0.0901(3)	0.4226(4)	0.1866(5)	0.053(3)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

of the non-hydrogen atoms, the positional parametrs of the hydrogen atoms, full lists of bond lengths and angles, and lists of calculated and observed structure factors have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgments

This work was supported in part by the C.N.R. (Rome) through its Centro di Studio sugli Stati Molecolari, Radicalici ed Eccitati, and through its Progetto Finalizzato Chimica Fine II.

References

[1] (a) H. van der Heijden, A.G. Orpen and P. Pasman, *J. Chem. Soc. Chem. Commun.*, (1985) 1576; (b) W.D. Harman and H. Taube, *J. Am. Chem. Soc.*, *109* (1987) 1883; (c) W.D. Harman and H. Taube, *J. Am. Chem. Soc.*, *110* (1988) 7555; (d) W.D. Harman and H. Taube, *J. Am. Chem. Soc.*, *110* (1988) 7906; (e) W.D. Harman, M. Gebhard and H. Taube, *Inorg. Chem.*, *29* (1990) 567; (f) K. Jonas, V. Wiskamp, Y.H. Tsay and C. Krüger, *J. Am. Chem. Soc.*, *105* (1983) 5480; (g) K. Jonas, G. Koepe, L. Schieferstein, R. Mynott and C. Krüger, *Angew. Chem.*, *95* (1983) 637, *Angew. Chem., Int. Ed. Engl.*, *22* (1983) 620; (h) K. Jonas, *J. Organomet. Chem.*, *400* (1990) 165.

[2] (a) G.F. Emerson, J.E. Mahler, R. Pettit and R. Collins, *J. Am. Chem. Soc.*, *86* (1964) 3590; (b) F.A. Cotton, B.G. DeBoer and T.J. Marks, *J. Am. Chem. Soc.*, *93* (1971) 5069; (c) R. Bau, J.C. Burt, S.A.R. Knox, R.M. Laine, R.P. Phillips and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1973) 726; (d) J.C. Burt, S.A.R. Knox and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1975) 731; (e) J. Evans, B.F.G. Johnson, J. Lewis and R. Watt, *J. Chem. Soc., Dalton Trans.*, (1974) 2368; (f) H. Wadepol, W. Galm and H. Pritakow, *Angew. Chem.*, *102* (1990) 701; (g) H. Wadepol, W. Galm and A. Wolf, *J. Organomet. Chem.*, *452* (1993) 193.

[3] (a) D.J. Brauer and C. Krüger, *Inorg. Chem.*, *15* (1976) 2511; (b) A. Salzer, T. Egolf, L. Linowsky and W. Petter, *J. Organomet. Chem.*, *221* (1981) 339; (c) A. Salzer, T. Egolf and W. von Philipsborn, *J. Organomet. Chem.*, *221* (1981) 351; (d) J.H. Bieri, T. Egolf, W. von Philipsborn, U. Piantini, R. Prewo, U. Ruppli and A. Salzer, *Organometallics*, *5* (1986) 2413; (e) J.W. Lauher, M. Elian, R.H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, *98* (1976) 3219.

[4] (a) M.J. Bennett, J.L. Pratt, K.A. Simpson, L.K.K. LiShingMan and J. Takats, *J. Am. Chem. Soc.*, *98* (1976) 4810; (b) R.G. Ball, F. Edelmann, Gong-Yu Kiel, J. Takats and R. Drews, *Organometallics*, *5* (1986) 829; (c) S.T. Astley and J. Takats, *J. Organomet. Chem.*, *363* (1989) 167.

[5] (a) W. Geibel, G. Wilke, R. Godard, C. Krüger and R. Mynott, *J. Organomet. Chem.*, *160* (1978) 139; (b) L. Elschenbroich, J. Heck, W. Massa and R. Schmidt, *Angew. Chem., Int. Ed. Engl.*, *22* (1983) 330.

[6] (a) B.F. Bush, V.M. Lynch and J.J. Lagowski, *Organometallics*, *6* (1987) 1267; (b) K. Jonas, *Pure Appl. Chem.*, *62* (1990) 1169.

[7] (a) E.E. Bunel, L. Valle, N.J. Jones, P.J. Carroll, C. Barra, M. Gonzales, N. Munoz, G. Visconti, A. Aizman and J.M. Manriquez, *J. Am. Chem. Soc.*, *110* (1988) 6596; (b) A. Miyake and A. Kanai, *Angew. Chem.*, *83* (1971) 851, *Angew. Chem., Int. Ed. Engl.*, *10* (1971) 801.

[8] (a) M.L.H. Green, N.D. Lowe and D. O'Hare, *J. Chem. Soc., Chem. Commun.*, (1986) 1547; (b) A. Ceccon, A. Gambaro, S. Santi, G. Valle and A. Venzo, *J. Chem. Soc., Chem. Commun.*, (1989) 51; (c) A. Ceccon, C.J. Elsevier, J.M. Ernsting, A. Gambaro, S. Santi and A. Venzo, *Inorg. Chim. Acta*, *204* (1993) 15; (d) A. Ceccon, A. Gambaro, S. Santi and A. Venzo, *J. Mol. Catal.*, *69* (1991) L1; (e) C. Bonifaci, A. Ceccon, A. Gambaro, P. Ganis, L. Mantovani, S. Santi and A. Venzo, *J. Organomet. Chem.*, *475* (1994) 267.

[9] R. Kudinov, P.V. Petrovskii, Yu.T. Struchkov and A.I. Yanovskii, *J. Organomet. Chem.*, *421* (1991) 91.

[10] K. Jonas, W. Rüsseler, C. Krüger and E. Raabe, *Angew. Chem.*, *88* (1986) 905, *Angew. Chem., Int. Ed. Engl.*, *25* (1986) 928.

[11] C. Bonifaci, A. Ceccon, A. Gambaro, P. Ganis, S. Santi, G. Valle and A. Venzo, *Organometallics*, *12* (1993) 4211.

[12] C. Bonifaci, A. Ceccon, A. Gambaro, S. Santi, A. Venzo and P. Ganis, *Xth FECHEM Conf. Organomet. Chem.*, Crete, Greece, Sept. 5–11, 1993, Abs. p. 96.

[13] L. Pauling, *The Nature of the Chemical Bond*, Cornell Univ. Press, Ithaca, NY, 1960.

[14] (a) H.A. Sheraga, *Biopolymers*, *22* (1983) 1; (b) G. Nemethy, M.S. Pottle and H.A. Sheraga, *J. Phys. Chem.*, *87* (1983) 1883.

[15] T. Cromer and J.T. Waber, *Acta Crystallogr.*, *18* (1965) 184.

[16] T. Cromer, *Acta Crystallogr.*, *18* (1965) 17.

[17] W. Sheldrick, *SHELX-76 Program for Crystal Structure Determination*, Cambridge University, England, 1976.