

Journal of Organometallic Chemistry, 420 (1991) 135–142
Elsevier Sequoia S.A., Lausanne
JOM 22115

Crystal structure and reactivity of $[(pp_3)Rh(H)(SeCH_3)]BPh_4$. An organometallic complex from metal-assisted Se–H activation

Massimo Di Vaira, Donella Rovai, Piero Stoppioni

Dipartimento di Chimica, Università di Firenze, Via Maragliano 77, 50144 Firenze (Italy)

and Maurizio Peruzzini

Istituto ISSECC, CNR, Via J. Nardi 39, 50132 Firenze (Italy)

(Received June 7th, 1991)

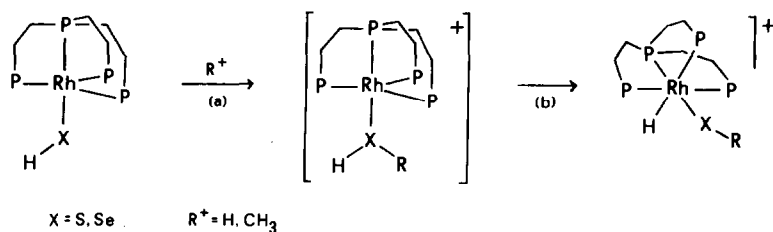
Abstract

The crystal structure of the hydride methylselenide derivative $[(pp_3)Rh(H)(SeCH_3)]BPh_4$ [$pp_3 =$ tris(2-(diphenylphosphino)ethyl)phosphine, $P(CH_2CH_2PPh_2)_3$] (obtained through an intramolecular oxidative addition following initial methylation of the hydroselenide complex $[(pp_3)RhSeH]$) has been determined through an X-ray diffraction study. The Rh atom is in an approximately octahedral environment, formed by three P atoms of the phosphine ligand and the Se atom in equatorial positions and the other P atom and the hydride ligand in apical positions. (The hydride ligand was not located in the X-ray study but there is evidence for its presence in the coordination sphere.) The compound can be readily transformed to the stable methylselenide $[(pp_3)Rh(SeCH_3)]$ and dimethylselenide $[(pp_3)Rh(Se(CH_3)_2)]BPh_4$ derivatives.

Introduction

Recently, there has been growing interest in mononuclear complexes containing thiolate (M–SR) and hydrosulfido (M–SH) groups because the reactivity of such ligands is significantly affected by the metal fragment to which they are bound [1]. Considerably less attention has been given to analogous compounds containing selenium [2] and tellurium [3], although interest in their chemistry arises from the opportunity to investigate possible changes in the reactivity of the M–XR group on changing the nature of the chalcogen atom X.

We have recently prepared a series of rhodium hydrochalcogenide complexes of formula $[(pp_3)RhXH]$ ($pp_3 =$ tris(2-(diphenylphosphino)ethyl)phosphine, $P(CH_2CH_2PPh_2)_3$; X = S, Se, Te) and investigated their reactions with electrophilic reagents (H^+ , CH_3^+) [4], which gave the rare octahedral Rh^{III} *cis*-hydride hydrochalcogenide or methylchalcogenide complexes $[(pp_3)Rh(H)(XR)]CF_3SO_3$ (X = S, Se. R = H, CH_3). In particular, there was evidence, consistent with recent



Scheme 1

results by Darensbourg and coworkers [5], that the formation of the hydride methylchalcogenide derivatives proceeded through an initial attack of CH_3^+ at the nucleophilic chalcogen atom, to form the trigonal bipyramidal $[(pp_3)Rh(HXCH_3)]^+$ transient cation (Scheme 1, (a)), and subsequent intramolecular oxidative addition of the $HXCH_3$ ligand to produce the stable octahedral Rh^{III} hydride methylchalcogenide derivative (Scheme 1, (b)). The final compounds were characterized spectroscopically, providing evidence for a highly stereospecific oxidative addition of the HXR fragment to the rhodium atom. An X-ray diffraction study on the *cis*-hydride methylselenide $[(pp_3)Rh(H)(SeCH_3)]BPh_4$ compound, which, to our knowledge, is the first hydride selenide complex among the few hydride chalcogenide metal derivatives so far reported [6], was carried out in order to obtain information on possible steric factors determining the stereoselectivity of such processes. Investigations on the reactivity of the above complex indicate that it will be a useful precursor for novel selenide derivatives.

Experimental section

All manipulations were carried out under purified nitrogen by standard Schlenk-line techniques. The solvents were reagent grade, and were dried by standard methods and freed from molecular oxygen immediately prior to use.

Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer using Nujol mulls between KBr plates. NMR spectra were collected on a Varian FT80 operating at 80 (1H) and 32.2 MHz (^{31}P). Positive ^{31}P chemical shifts are to high frequency of an 85% H_3PO_4 external standard at 0.0 ppm. Conductivity measurements were carried out with a WTW Model CBR/B conductivity bridge, with ca. 10^{-3} M solutions in 1,2-dichloroethane.

The tetraphenylborate salt of the *cis*-hydride methylselenide cation [4] gave crystals suitable for the X-ray study. These were obtained by slow diffusion of absolute ethanol under a stream of nitrogen into a tetrahydrofuran solution of $[(pp_3)Rh(H)(SeCH_3)]CF_3SO_3$ containing two equivalents of $NaBPh_4$. The $[(pp_3)Rh(H)(SeCH_3)]BPh_4$ complex gave satisfactory elemental analyses and a Λ_M value typical of 1:1 electrolytes in dichloroethane solution. The IR and 1H and ^{31}P NMR spectral data for the compound are indistinguishable from those of the $CF_3SO_3^-$ salt [4].

Synthesis of the compounds

$[(pp_3)Rh(SeCH_3)]$. Sodium ethoxide (0.3 mmol) in absolute ethanol (0.18 M) was added to a solution of $[(pp_3)Rh(H)(SeCH_3)]CF_3SO_3$ (0.30 g, 0.3 mmol) in

tetrahydrofuran (20 ml). The yellow solution immediately turned to red. Absolute ethanol was added and the solution was concentrated under nitrogen to yield red crystals of $[(pp_3)Rh(SeCH_3)]$. Yield 60%. Anal. Found: C, 59.41; H, 5.32; Se, 8.94. $[(pp_3)Rh(SeCH_3)]$, $C_{43}H_{45}P_4RhSe$ calc.: C, 59.53; H, 5.23; Se, 9.10%.

$[(pp_3)Rh\{Se(CH_3)_2\}]BPh_4$. CH_3I (0.01 ml, 0.16 mmol) was added to a suspension of $[(pp_3)Rh(SeCH_3)]$ (0.1 g, 0.14 mmol) in tetrahydrofuran (10 ml). The solid dissolved upon stirring (1 h) of the mixture, and microcrystalline $[(pp_3)Rh\{Se(CH_3)_2\}]BPh_4$ was obtained by adding $NaBPh_4$ (0.07 g, 0.2 mmol) in tetrahydrofuran (5 ml) followed by benzene (20 ml) and concentrating the resulting solution. The compound may be recrystallized from tetrahydrofuran/benzene. Yield 75%. Anal. Found: C, 67.86; H, 5.82; Se, 6.41. $[(pp_3)Rh\{Se(CH_3)_2\}]BPh_4$, $C_{68}H_{68}BP_4RhSe$ calc.: C, 67.96; H, 5.70; Se, 6.57%.

Alternative method

A suspension of potassium t-butoxide (0.07 g, 0.6 mmol) in tetrahydrofuran (10 ml) was added with stirring at $0^\circ C$ to a solution of $[(pp_3)Rh(H)(SeCH_3)]BPh_4$ (0.36 g, 0.3 mmol) in dichloromethane (20 ml); the color of the solution turned immediately from yellow to red. Microcrystalline $[(pp_3)Rh\{Se(CH_3)_2\}]BPh_4$ was obtained by adding benzene (30 ml). The compound was recrystallized from dichloromethane/benzene. Yield 55%.

X-Ray crystallographic studies

Crystal data for $[(pp_3)Rh(H)(SeCH_3)]BPh_4$ and experimental details are given in Table 1. Cell constants were obtained from least-squares refinement of the setting angles of 24 reflections in the range $24 \leq 2\theta \leq 32^\circ$. The crystals, gave practically no measurable intensities at $2\theta > 45^\circ$. Data were recorded at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated $Mo-K_\alpha$ radiation. Three reflections monitored during data collection showed no variation in intensities. The data were corrected for Lorentz and polarization effects and for absorption by an empirical procedure after the structure had been solved [7]. No correction for extinction was made.

The structure was solved by Patterson and Fourier methods. In the final model all atoms except the B and H atoms were refined anisotropically. Hydrogen atoms were included in their calculated positions ($C-H = 0.96 \text{ \AA}$) with fixed temperature

Table 1

Crystal data for $[(pp_3)Rh(H)(SeCH_3)]BPh_4$

$C_{67}H_{66}BP_4RhSe$	V 2896(3) \AA^3
$F_w = 1198.84$	$Z = 2$
a 13.121(11) \AA	Space group $P\bar{1}$ (No. 2)
b 13.887(11) \AA	
c 16.092(7) \AA	λ 0.71069 \AA
α 83.89(6) $^\circ$	$d_{\text{calc.}}$ 1.362 g cm^{-3}
β 85.56(6) $^\circ$	$R^a = 0.072$
γ 84.68(7) $^\circ$	$R_w^b = 0.075$

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b R_w = [\sum_w (|F_o| - |F_c|)^2 / \sum_w (F_o)^2]^{1/2}.$$

Table 2

Positional parameters and isotropic thermal parameters for $[(pp_3)Rh(H)(SeCH_3)]BPh_4^{a-c}$

Atom	x	y	z	U_{eq}/U (\AA^2)
Rh	1168(1)	2142(1)	3176(1)	39(1)
Se	948(2)	843(1)	4379(1)	83(1)
P(1)	1445(3)	3342(3)	2182(3)	50(2)
P(2)	-528(3)	2816(3)	3218(3)	52(3)
P(3)	1174(3)	1140(3)	2045(3)	50(2)
P(4)	2914(3)	2052(3)	3298(2)	45(2)
C(1)	400(11)	4289(10)	2223(10)	63(6)
C(2)	-604(10)	3786(11)	2339(10)	65(6)
C(3)	1475(12)	2940(10)	1139(8)	56(5)
C(4)	1801(10)	1830(9)	1156(8)	49(5)
C(5)	2722(10)	3769(10)	2253(9)	53(5)
C(6)	3445(10)	2890(9)	2445(8)	48(5)
C(7)	536(25)	1440(18)	5407(14)	226(6)
C(11)	-1014(8)	3447(9)	4128(7)	68(6)
C(12)	-384(8)	3610(9)	4749(7)	217(6)
C(13)	-796(8)	4087(9)	5436(7)	285(6)
C(14)	-1838(8)	4400(9)	5500(7)	144(6)
C(15)	-2468(8)	4236(9)	4878(7)	182(6)
C(16)	-2056(8)	3759(9)	4192(7)	201(6)
C(21)	-1589(8)	2107(7)	3138(7)	69(6)
C(22)	-2269(8)	2316(7)	2506(7)	105(6)
C(23)	-3128(8)	1792(7)	2517(7)	132(6)
C(24)	-3306(8)	1058(7)	3160(7)	147(6)
C(25)	-2625(8)	849(7)	3792(7)	150(6)
C(26)	-1767(8)	1373(7)	3781(7)	103(6)
C(31)	-24(7)	863(6)	1671(5)	63(5)
C(32)	-550(7)	133(6)	2131(5)	69(6)
C(33)	-1440(7)	-151(6)	1841(5)	95(6)
C(34)	-1804(7)	295(6)	1091(5)	138(6)
C(35)	-1278(7)	1026(6)	630(5)	148(6)
C(36)	-388(7)	1310(6)	920(5)	112(6)
C(41)	1867(7)	-41(7)	2037(5)	52(5)
C(42)	2340(7)	-353(7)	1294(5)	76(5)
C(43)	2779(7)	-1306(7)	1280(5)	104(6)
C(44)	2746(7)	-1947(7)	2009(5)	101(6)
C(45)	2273(7)	-1635(7)	2751(5)	94(6)
C(46)	1834(7)	-682(7)	2765(5)	72(6)
C(51)	3708(6)	908(6)	3242(5)	47(5)
C(52)	4123(6)	594(6)	2482(5)	64(6)
C(53)	4686(6)	-308(6)	2470(5)	81(6)
C(54)	4833(6)	-896(6)	3217(5)	91(6)
C(55)	4417(6)	-582(6)	3976(5)	91(6)
C(56)	3855(6)	320(6)	3988(5)	75(6)
C(61)	3374(7)	2495(6)	4213(6)	48(5)
C(62)	4428(7)	2534(6)	4249(6)	78(6)
C(63)	4808(7)	2887(6)	4933(6)	108(6)
C(64)	4133(7)	3202(6)	5581(6)	141(6)
C(65)	3079(7)	3163(6)	5546(6)	218(6)
C(66)	2699(7)	2810(6)	4862(6)	163(6)
C(71)	6378(6)	7024(7)	610(5)	42(5)
C(72)	6406(6)	7971(7)	816(5)	75(6)
C(73)	5854(6)	8739(7)	373(5)	109(6)

Table 2 (continued)

Atom	x	y	z	$U_{eq} / U (\text{\AA}^2)$
C(74)	5272(6)	8560(7)	-275(5)	112(6)
C(75)	5244(6)	7613(7)	-481(5)	95(6)
C(76)	5796(6)	6844(7)	-39(5)	70(5)
C(81)	6059(6)	5702(5)	1942(5)	46(5)
C(82)	5167(6)	6267(5)	2170(5)	55(5)
C(83)	4493(6)	5915(5)	2821(5)	67(6)
C(84)	4710(6)	4997(5)	3243(5)	73(6)
C(85)	5602(6)	4432(5)	3015(5)	65(5)
C(86)	6276(6)	4784(5)	2364(5)	72(5)
C(91)	7931(7)	6465(6)	1652(5)	47(5)
C(92)	8623(7)	7024(6)	1158(5)	60(5)
C(93)	9459(7)	7331(6)	1513(5)	76(6)
C(94)	9602(7)	7080(6)	2361(5)	106(6)
C(95)	8910(7)	6521(6)	2855(5)	101(6)
C(96)	8074(7)	6213(6)	2500(5)	73(6)
C(101)	7361(6)	5166(5)	632(5)	53(5)
C(102)	8404(6)	4995(5)	405(5)	43(5)
C(103)	8742(6)	4273(5)	-117(5)	62(5)
C(104)	8036(6)	3723(5)	-412(5)	85(6)
C(105)	6992(6)	3894(5)	-185(5)	99(6)
C(106)	6654(6)	4615(5)	337(5)	84(6)
B	6921(12)	6091(11)	1210(10)	46(4)

^a Positional parameters are multiplied by 10^4 and temperature factors by 10^3 ; standard deviations on the least significant digit(s) are in parentheses. ^b Atoms Rh-C(66) belong to the cation and C(71)-B to the BPh_4^- anion. ^c The equivalent isotropic thermal parameter is defined as $(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$; the isotropic temperature factor (B atom only) is of the form $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$.

factors 20% larger than the equivalent isotropic temperature factors of the corresponding C atoms.

However, the hydride ligand, not located on ΔF maps, was not included in the model. Both the methyl and phenyl groups were treated as rigid bodies. The principal computer programs used in the calculations are listed in refs. 7-9. Scattering factors were from refs. 8 (C, H, B, P) and 10a (Rh, Se), those for Rh and Se being corrected for anomalous dispersion [10b]. Final atomic coordinates for nonhydrogen atoms are listed in Table 2, and selected bond distances and angles

Table 3

Selected bond distances (\AA) and angles ($^\circ$) for $[(\text{pp}_3)\text{Rh}(\text{H})(\text{SeCH}_3)]\text{BPh}_4$

Rh-Se	2.521(2)	Rh-P(3)	2.406(4)
Rh-P(1)	2.218(4)	Rh-P(4)	2.306(4)
Rh-P(2)	2.332(4)	Se-C(7)	1.95(2)
Se-Rh-P(1)	175.2(1)	P(1)-Rh-P(4)	85.1(1)
Se-Rh-P(2)	97.1(1)	P(2)-Rh-P(3)	100.6(2)
Se-Rh-P(3)	98.3(1)	P(2)-Rh-P(4)	157.9(2)
Se-Rh-P(4)	91.6(1)	P(3)-Rh-P(4)	98.2(1)
P(1)-Rh-P(2)	84.9(1)	Rh-Se-C(7)	109.9(7)
P(1)-Rh-P(3)	85.6(1)		

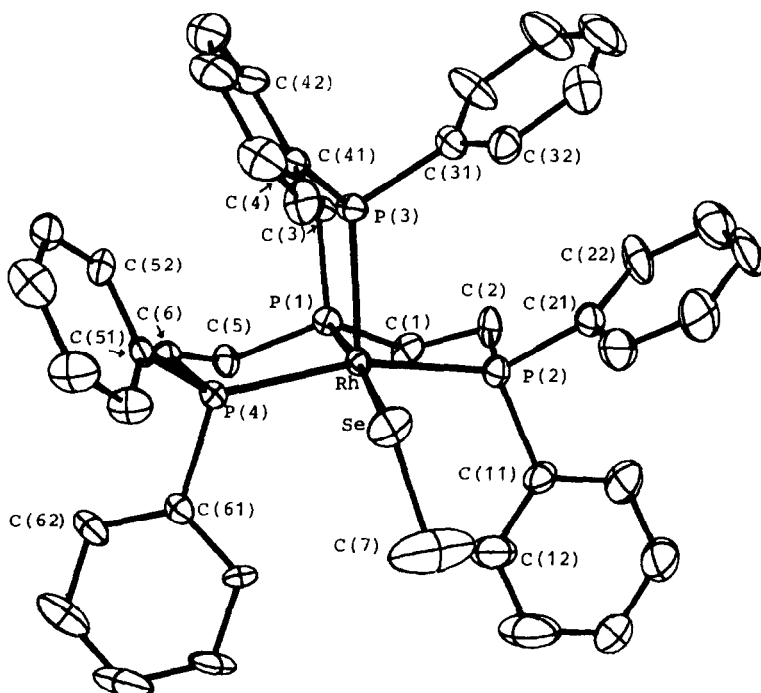


Fig. 1. Perspective view of the $[(pp_3)Rh(H)(SeCH_3)]^+$ cation, with 20% probability ellipsoids. Only two carbon atoms in each phenyl ring are labeled for clarity.

in Table 3. A complete list of bond lengths and angles, tables of hydrogen position and thermal parameters, and a list of observed and calculated structure factors are available from the authors.

Results and discussion

In the structure of $[(pp_3)Rh(H)(SeCH_3)]BPh_4$, formed by $[(pp_3)Rh(H)(SeCH_3)]^+$ cations and BPh_4^- anions, the arrangement of the nonhydrogen donor atoms about the metal atom in the cation (Fig. 1 and Table 3) is approximately square pyramidal, with the Se atom, the central phosphorus and two peripheral P atoms of the phosphine ligand in the equatorial positions and the remaining P atom [P(3)] in the apical position. This arrangement is notably different from that observed for the same donor atoms in the parent complex $[(pp_3)RhSeH]$, which possesses crystallographic C_3 symmetry [4]. The hydride ligand, which could not be located from Fourier difference maps although its presence is implied by the NMR data and the other properties of the compound, must complete an irregular octahedron about the metal atom, lying *trans* to P(3). The P(3) atom forms a longer Rh–P bond (by an average of 0.09 Å) than the other two peripheral P atoms, in agreement with previous observations on hydride complexes with phosphine tripod ligands [11,12]. The other distances to the metal formed by the nonhydrogen donors in the present compound are comparable to those in the

parent $[(pp_3)RhSeH]$ [4]. As found for other complexes in which a tripod ligand like pp_3 is forced to span two faces of an octahedron about the metal atom [13,14], four phenyl groups in the present cation are almost parallel in pairs (Fig. 1) and are all approximately parallel to the direction defined by the P(1), Rh, and Se atoms. The two remaining phenyl groups are almost perpendicular to the other four and to the previous direction. They are affected by high librational motion normal to the planes of the rings, which may have contributed, along with the similarly high thermal motion of the CH_3 group, to the lowering of the quality of the diffraction data. These two phenyl groups efficiently shield the position occupied by the hydride ligand, and may prevent bulkier ligands from occupying that position.

The *cis*-hydride methylselenide derivative $[(pp_3)Rh(H)(SeCH_3)]BPh_4$ dissolved in tetrahydrofuran reacts with the stoichiometric amount of sodium ethoxide to yield a microcrystalline compound of formula $[(pp_3)Rh(SeCH_3)]$; the complex which is stable under nitrogen, is sparingly soluble in chlorinated solvents. Its proton NMR spectrum in $CDCl_3$ exhibits, in addition to the usual patterns due to the protons of the pp_3 ligand, a resonance ($\delta = 1.32$ ppm) that on the basis of its intensity and chemical shift can be attributed to the CH_3 hydrogen atoms. Highly diagnostic for the solution stereochemistry of the compound is its $^{31}P\{^1H\}$ NMR spectrum, which consists of a first order AM_3X spin system ($\delta_A = 145.41$, $\delta_M = 47.07$ ppm; $J(P_A-Rh) 109.5$, $J(P_M-Rh) 141.7$, $J(P_A-P_M) 17.0$ Hz), consistent with a trigonal bipyramidal geometry around the metal [4]. The methyl selenide derivative $[(pp_3)Rh(SeCH_3)]$ reacts with CH_3I to yield the $[(pp_3)Rh(Se(CH_3)_2)]BPh_4$ complex. Such dimethyl selenoether derivative is stable under nitrogen in the solid state and in solution. It is soluble in chlorinated solvents, acetone, and tetrahydrofuran; it behaves as a 1:1 electrolyte in dichloroethane. Its 1H NMR spectrum in $CDCl_3$ exhibits a signal ($\delta 1.46$ ppm; $J(H-Rh) 2.5$ Hz) that can be assigned to two methyl groups bound to selenium, as suggested by the value of the chemical shift and the intensity. The $^{31}P\{^1H\}$ NMR spectrum of the compound exhibits an AM_3X spin system ($\delta_A 147.21$, $\delta_M 49.82$ ppm; $J(P_A-Rh) 110.5$, $J(P_M-Rh) 142.5$, $J(P_A-P_M) 17.0$ Hz) that again points to a trigonal bipyramidal geometry [4]. The same dimethylselenide derivative is also obtained by treating the hydrido methylselenide $[(pp_3)Rh(H)(SeCH_3)]BPh_4$ with a twofold excess of potassium *t*-butoxide. This unexpected formation of the dimethylselenide is likely to occur through decomposition of *t*-butoxide; alkoxides of tertiary alcohols are known to undergo cleavage reactions of the carbanions, especially in halogenated solvents [15].

This study has shown that upon intramolecular $HSeCH_3$ oxidative addition the pp_3 ligand undergoes a conformational rearrangement, from C_3 to approximate C_s symmetry, in order to adopt a pseudooctahedral coordination geometry. The two sites unoccupied by pp_3 in the coordination polyhedron have different steric requirements, that lying *trans* to a terminal P atom being suitable for comparatively small ligands. This may be at the origin of the stereospecificity observed for the oxidative addition process [4]. Although structural information is not available for other pp_3 complexes of rhodium(III), the above view is supported by the results obtained for closely related np_3 rhodium complexes ($np_3 = N(CH_2CH_2PPh_2)_3$), in which the oxidative additions promoted by the $(np_3)Rh$ fragment invariably involve the smaller group coordinated *trans* to a terminal P atom [16]. Finally, the present hydride methylselenide has proved to be a suitable precursor for the methylse-

lenide complex, which is easily converted into the stable dimethylselenide derivative.

Acknowledgement

We thank the Italian Ministero dell' Università e della Ricerca Scientifica e Tecnologica for financial support.

References

- 1 See for example: (a) D.P. Klein, G.M. Kloster and R.G. Bergman, *J. Am. Chem. Soc.*, 112 (1990) 2022; (b) P.M. Treichel, M.S. Smidt and R.A. Crane, *Inorg. Chem.*, 30 (1991) 379; (c) J.J. Garcia, H. Torrens, H. Adams, N.A. Bailey and P.M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1991) 74.
- 2 (a) E.A.V. Ebsworth, R.O. Gould, R.A. Mayo and M. Walkinshaw, *J. Chem. Soc., Dalton Trans.*, (1987) 2831; (b) F. Bottomley, T.T. Chin, G.O. Egharevba, L.M. Kane, D.A. Pataki and P.S. White, *Organometallics*, 7 (1988) 1214.
- 3 W.A. Herrmann, C. Hecht, E. Herdtweck and H.J. Kneuper, *Angew. Chem., Int. Ed. Engl.*, 26 (1987) 133.
- 4 M. Di Vaira, M. Peruzzini and P. Stoppioni, *Inorg. Chem.*, 30 (1991) 1001.
- 5 M.Y. Darensbourg, W.F. Liaw and C.G. Riordan, *J. Am. Chem. Soc.*, 111 (1989) 8051.
- 6 (a) H. Singer and G. Wilkinson, *J. Chem. Soc. A*, (1968) 2516; (b) M.H. Stiddard and R.E. Townsend, *J. Chem. Soc. A*, (1970) 2719; (c) D.W. Stephen, *Inorg. Chem.*, 23 (1984) 2207; (d) R.A. Henderson, D.L. Hughes, R.L. Richards and C. Shortman, *J. Chem. Soc., Dalton Trans.*, (1987) 1115; (e) T.E. Burrow, A. Hills, D.L. Hughes, J.D. Lane, N.J. Lazarowich, M.J. Maguire, R.H. Morris and R.L. Richards, *J. Chem. Soc., Chem. Commun.*, (1990) 1757.
- 7 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 39 (1983) 158.
- 8 G.M. Sheldrick, *SHELX*, a Program for Crystal Structure Determination, University of Cambridge, Cambridge, England, 1977.
- 9 C.K. Johnson, Oak Ridge National Laboratory, Oak Ridge TN, USA, 1965, ORNL 3794.
- 10 International Tables for X-ray Crystallography; Kynoch Press, Birmingham, UK, 1974: (a) Vol. IV, p. 99; (b) Vol. IV, p. 149.
- 11 C. Bianchini, D. Masi, A. Meli, M. Peruzzini, J.A. Ramirez, A. Vacca and F. Zanobini, *Organometallics*, 8 (1989) 2179.
- 12 M. Di Vaira, M. Peruzzini, F. Zanobini and P. Stoppioni, *Inorg. Chim. Acta*, 69 (1983) 37.
- 13 C. Mealli, P.L. Orioli and L. Sacconi, *J. Chem. Soc. A*, (1971) 2691.
- 14 C. Bianchini, D. Masi, A. Meli, M. Peruzzini and F. Zanobini, *J. Am. Chem. Soc.*, 110 (1988) 6411.
- 15 J. March, *Advanced Organic Chemistry*, Wiley Interscience, New York, 1985, p. 903.
- 16 C. Bianchini, C. Mealli, M. Peruzzini and F. Zanobini, *J. Am. Chem. Soc.*, 109 (1987) 5548.