

Reactions of 3-Pyridyldiphenylphosphine with $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ and $\text{Co}_2(\text{CO})_8$. Crystallographic and Catalytic Studies of $\text{Rh}(\text{CO})\text{Cl}(\text{3-PyPPh}_2)_2$

Riitta H. Laitinen,^{a,*} Jaakko Soininen,^a Pekka Suomalainen,^b Tapani A. Pakkanen,^b Markku Ahlgrén^b and Jouni Pursiainen^a

^aUniversity of Oulu, Department of Chemistry, PO Box 3000, FIN-90401 Oulu, Finland and ^bUniversity of Joensuu, Department of Chemistry, PO Box 111, FIN-80101 Joensuu, Finland

Laitinen, R. H., Soininen, J., Suomalainen, P., Pakkanen, T. A., Ahlgrén, M. and Pursiainen, J., 1999. Reactions of 3-Pyridyldiphenylphosphine with $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ and $\text{Co}_2(\text{CO})_8$. Crystallographic and Catalytic Studies of $\text{Rh}(\text{CO})\text{Cl}(\text{3-PyPPh}_2)_2$. – Acta Chem. Scand. 53: 335–339. © Acta Chemica Scandinavica 1999.

Catalytically active metals Rh^I and Co^0 were used in the preparation of complexes of 3-pyridyldiphenylphosphine. The structure of $\text{Rh}(\text{CO})\text{Cl}(\text{3-PyPPh}_2)_2$ was determined by X-ray crystallography. $\text{Rh}(\text{CO})\text{Cl}(\text{3-PyPPh}_2)_2$ crystallizes in the space group $P2_1/n$ with cell dimensions of $a=1.1677(3)$ nm, $b=2.3536(7)$ nm, $c=1.2215(3)$ nm, $\beta=112.13(2)^\circ$, $z=4$, $V=3.1097(14)$ nm³ and $R=0.0405$. Characterizations of $\text{Co}_2(\text{CO})_8(\text{3-PyPPh}_2)_2$ were based on spectroscopic data and the elemental analysis. Activities of the prepared complexes were tested in hydroformylation reaction of 1-hexene.

Pyridylphosphines¹ and their derivatives have been investigated during the last five decades. The field expanded in the 1980s when the combination of ³¹P NMR and single-crystal X-ray analysis became increasingly available. The possibility of modifying the electronic and the steric properties of these ligands and their rich coordination chemistry offer an interesting area of research into complexation and applications, for example in catalysis.

The main application of pyridylphosphines has been catalysis. It has been suggested that the pyridylphosphine ligand plays an essential role in carbonylation of alkynes^{2,3} both as a chelating P–N ligand in the selectivity-determining step and as a monocoordinated ligand in the rate-determining step of the catalytic cycle. For example in the methoxycarbonylation of propyne to give methyl methacrylate^{2,3} a palladium complex of the 2-pyridylphosphine ligand showed a remarkable increase in activity and selectivity compared to a palladium complex of triphenylphosphine. A lower rate enhancement was observed with 3-pyridylphosphine, while the results with 4-pyridylphosphine were very similar to those of PPh_3 .^{2,3}

In hydroformylation of oct-1-ene^{4,5} rhodium-coordinated pyridylphosphines are used as amphiphilic catalysts. With this type of catalyst the system is homogeneous

during the hydroformylation reaction, but after the reaction the catalyst can be extracted by water of a certain pH and reused. In this reaction^{4,5} 3- and 4-pyridylphosphines did not affect the selectivity, but the reaction rates were up to two times faster than with triphenylphosphine. This has been explained by the electron-withdrawing nature of the pyridyl ring.

The synthesis of 3-pyridyldiphenylphosphine⁶ was first reported in 1986; other methods for preparing pyridylphosphines have also been developed.^{4,7–11} Of these, we used a modification of the low-temperature lithiation procedure in the preparation of 3-pyridyldiphenylphosphine.⁹ The coordination chemistry of 3-pyridyldiphenylphosphine has remained quite unknown except for the original report of the Mo complex. In this work we have prepared and characterized the 3-pyridyldiphenylphosphine ligand and its Rh^I and Co^0 complexes.

Experimental

NMR spectra were recorded on Bruker AM200 and Bruker DPX400 spectrometers. ¹H and ¹³C spectra were referenced to TMS, and ³¹P spectra to 85% H_3PO_4 . GLC spectra were collected using a HP 5890 series II chromatograph coupled with a computer. Chromatographs were equipped with a CP-SIL 5 CB column (length 50 m, film thickness 5.00 μm , inside and outside diameters 0.53 mm

* To whom correspondence should be addressed.

and 0.71 mm, respectively). Elemental analyses were recorded on a Perkin Elmer 2400 series II CHNS/O analyzer, single-crystal X-ray determinations on a Siemens R3m diffractometer and FTIR spectra on a Bruker IFS 66 instrument. Commercially available reagents were used without further purification. Diethylether and tetrahydrofuran were dried and distilled over sodium benzophenone ketyl. Acids and bases were degassed before use. All syntheses were carried out into an argon atmosphere using standard Schlenk techniques.

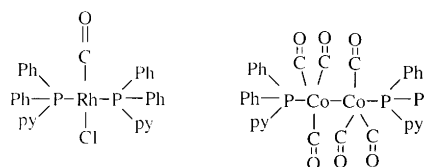
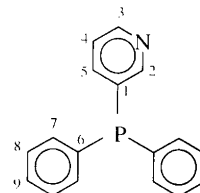
3-PyPPh₂ (1). 3-BrC₅H₄N (1.5 ml, 15.0 mmol) was lithiated with n-BuLi (6.0 ml, 15.0 mmol, 2.5 M in hexane) in Et₂O at -100 °C. The yellow solution was stirred at -100 °C 1 h before adding PPh₂Cl (2.8 ml, 15.0 mmol) in Et₂O. The mixture was stirred for a further 1 h at -100 °C and warmed slowly to room temperature. The light yellow mixture was extracted with H₂SO₄ (2 M) and the aqueous layer was made alkaline with NaOH. The brownish oily raw product was extracted from the aqueous phase with tetrahydrofuran and purified by column chromatography (silica gel, 5% MeOH in CH₂Cl₂). The 3-pyridyldiphenylphosphine (2.48 g, 9.4 mmol, 63%) was stored under argon. Anal. Found: C 73.4; H 5.2; N 4.1%. Calcd. for C₁₇H₁₄NOP: C 73.1; H 5.1; N 5.0%. ¹H NMR (400 MHz, CDCl₃): δ 8.6 ppm (H₃, d, ³J_{H-H} 4.4 Hz, 1 H), 8.5 (H₂, d, ⁴J_{H-H} 1.4 Hz, 1 H), 7.6 (H₅, tt, ³J_{H-H} 7.2 Hz, ⁴J_{H-H} 2.0 Hz, 1 H), 7.3–7.4 (H₇₋₉, m, 10 H), 7.2 (H₄, dd, ³J_{H-H} 7.8 Hz and 5.0 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 154.1 ppm (C₂, d, ¹J_{C-H} 151.8 Hz, ²J_{C-P} 23.8 Hz, 1C), 149.5 (C₃, s, ¹J_{C-H} 179.0 Hz, 1C), 140.9 (C₅, d, ¹J_{C-H} 178.6 Hz, ²J_{C-P} 15.8 Hz, 1C), 135.6 (C₆, d, ¹J_{C-P} 10.3 Hz, 2C), 133.6 (C₇, d, ¹J_{C-H} 159.7 Hz, ²J_{C-P} 19.9 Hz, 4C), 131.9 (C₁, d, ¹J_{C-P} 9.7 Hz, 1C), 129.1 (C₉, s, ¹J_{C-H} 160.7 Hz, 2C), 128.6 (C₈, d, ¹J_{C-H} 160.9 Hz, ³J_{C-P} 6.7 Hz, 4C), 123.4 (C₄, s, ¹J_{C-H} 167.1 Hz, 1C). ³¹P{¹H}-NMR (162 MHz; CDCl₃): δ -11.2 ppm (s). The 3-position of the nitrogen atom in the pyridine ring was confirmed e.g. by decoupling experiments.

Rh(CO)Cl(3-PyPPh₂)₂ (2). A yellow solution of Rh₂(μ-Cl)₂(CO)₄ (0.40 g, 1.0 mmol) in tetrahydrofuran (40 ml) was stirred for ½ h, after which the ligand, 3-PyPPh₂ (1.07 g, 4.0 mmol) in tetrahydrofuran (5 ml), was added dropwise. The yellow solution was stirred for 3½ h at room temperature. From this solution the product was precipitated by addition of acetone. The product (2) was filtered and dried in a vacuum (0.93 g, 1.3 mmol, 65%). Single crystals for crystallographic measurements were obtained from methylenechloride. M.p. 167 °C. Anal. Found: C 60.4; H 3.9; N 4.0%. Calcd. for C₃₅H₂₈ClN₂O₂Rh: C 60.7; H 4.0; N 4.1%. ¹H NMR (400 MHz, CDCl₃): δ 8.8 ppm [H₂, s (br), 1 H], 8.6 (H₃, d, ³J_{H-H} 4.8 Hz, 1 H), 7.7 [H₅, d (br), ³J_{H-H} 3.2 Hz, 1 H], 7.5–7.4 (H₇₋₉, m, 10 H), 7.3 (H₄, dd, ³J_{H-H} 8.0 Hz and 4.8 Hz, 1 H). ¹³C{¹H}-NMR (100 MHz,

CDCl₃): δ 154.4 ppm (C₂, s, 1C), 150.8 (C₃, s, 1C), 142.5 (C₅, s, 1C), 134.5 (C₇, s, 4C), 132.4 (C₆, s, 1C), 131.6 (C₁, s, 1C), 130.7 (C₉, s, 2C), 128.5 (C₈, s, 4C), 123.0 (C₄, s, 1C). ³¹P{¹H}-NMR (162 MHz; CDCl₃): δ 26.3 ppm (d, ¹J_{Rh-P} 117 Hz). IR (CH₂Cl₂ solution): 1982 cm⁻¹ (s), 1569 (w), 1438 (s), 1402 (w).

Co₂(CO)₆(3-PyPPh₂)₂ (3). Co₂(CO)₈ (0.66 g, 1.9 mmol) and 3-PyPPh₂ (1.01 g, 3.8 mmol) were dissolved in 12 ml and 10 ml tetrahydrofuran, respectively. The ligand was added to the solution of metalcarbonyl dropwise. The mixture was stirred overnight. The brown precipitate was filtered off, washed with tetrahydrofuran, and the product (3) (1.02 g, 2.3 mmol, 60.5%) was dried in vacuum. M.p. 156 °C. Anal. Found: C 58.1; H 3.4; N 3.4%. Calcd. for C₄₀H₂₈Co₂N₂O₆P₂: C 59.1; H 3.5; N 3.5%. ¹H NMR (400 MHz, CDCl₃): δ 8.8 ppm (H₂, br, 1 H), 8.6 (H₃, br, 1 H), 7.7 (H₅, br, 1 H), 7.5 (H₇₋₉, br, 10 H), 7.4 (H₄, br, 1 H). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 201.4 ppm (-CO, s, 1C), 153.0 (C₂, s, 1C), 151.2 (C₃, s, 1C), 140.9 (C₅, s, 1C), 133.1 (C₇, s, 4C), 132.4 (C₆, s, 2C), 132.1 (C₁, s, 1C), 130.9 (C₉, s, 2C), 128.9 (C₈, s, 4C), 123.6 (C₄, s, 1C). ³¹P{¹H}-NMR (162 MHz; CDCl₃): δ 64.1 ppm (s). IR (CH₂Cl₂ solution): 2038 cm⁻¹ (w), 1983 (w), 1961 (s).

The schematic structures of 3-pyridyldiphenylphosphine and its Rh^I and Co⁰ complexes are presented in Scheme 1. The numbers shown in the structure of the ligand present the NMR data.



Scheme 1. The schematic presentation of 3-pyridyldiphenylphosphine and its Rh^I and Co⁰ complexes.

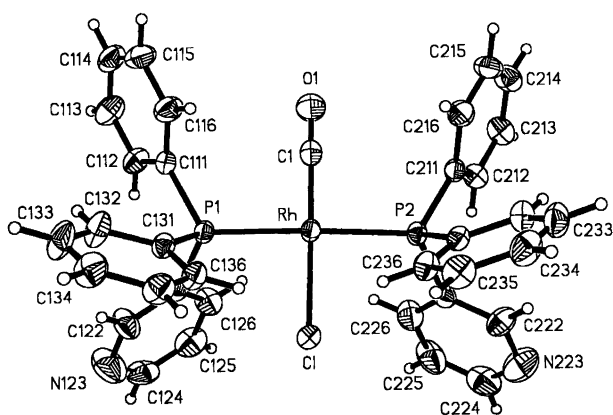
Crystallography. The yellow crystals of Rh(CO)Cl(3-PyPPh₂)₂ were obtained by slow evaporation of a dichloromethane solution. Diffraction data were collected at 293 K using graphite-monochromated Mo K_α radiation (λ = 71.073 pm). Crystal data and data collection parameters are compiled in Table 1. A total of 9420 reflections were recorded in the range 2.06 < θ < 30.0°.

Table 1. Crystallographic data.

Chemical formula	C ₃₅ H ₂₈ ClN ₂ O ₂ Rh
Molecular weight/g mol ⁻¹	692.89
Crystal size/mm	0.45 × 0.45 × 0.40
Color	Yellow
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions/nm, °	a = 1.1677(3) b = 2.3536(7) c = 1.2215(3) β = 112.13(2)
Volume/nm ³	3.1097(14)
Z	4
Density _{calc.} /Mg m ⁻³	1.480
Absorption coefficient μ/mm ⁻¹	0.769
F(000)	1408
θ-Range/°	2.06–30.00
No. of collected reflections	9420
No. of independent reflections	9035
Final R-indices [I > 2σ(I), 5997 refl.]	R = 0.0405, wR ² = 0.0898
Goodness of fit	1.043
T/K	293(2)
λ/pm	71.073 Mo K _α
Absorption correction	ψ-scan T _{min} /T _{max} 0.179/0.211

$$w = 1/[\sigma^2(F_{\text{obs}}^2) + (0.04P)^2] \text{ and } P = (F_{\text{obs}}^2 + 2F_{\text{calc}}^2)/3.$$

The structure was solved by direct methods using the Siemens SHELXTL-Plus program package¹² and refined on F^2 using SHELXL-93.¹³ Hydrogen atoms were located from difference Fourier maps, and they indicated the N-atom positions of the pyridyl rings together with bond lengths as presented in Fig. 1. The thermal factors of the N atoms, however, are high, and indicate six-fold statistical disorder of these atoms. Attempts to include disorder models did not improve the results, and they were excluded in the final refinement, where the non-hydrogen atoms were refined anisotropically and the H atoms were placed at calculated positions with fixed isotropic thermal parameters (C–H 96 pm and $U = 1.2U_{\text{eq}}$ parent atoms). Fractional coordinates and equivalent isotropic factors are listed in Table 2. Selected bond lengths and angles are listed in Table 3.

Fig. 1. The crystal structure of Rh(CO)Cl(3-PyPPh₂)₂.

Catalytic experiments. 1-Hexene hydroformylation reactions were conducted in 100-ml Berghof autoclaves with 60-ml teflon liners. The reactor was charged under a nitrogen purge with substrate, rhodium catalyst, ligand and with an internal standard, cyclohexane. The autoclave was then sealed and pressurized using a mixture of H₂–CO (in the ratio of 1:1) to 20 bar. The autoclave was heated to 100 °C, controlled and monitored by an internal thermocouple. After 4 h reaction the autoclave was cooled and brought to normal atmospheric pressure. Reaction mixtures were analyzed by GLC to determine the product distribution. The reproducibility of the system was confirmed by accomplishing the tests twice. To ensure the purity of the reaction vessel, blank runs were carried out between reactions.

Results and discussion

Pyridylphosphines have shown a distinct potential in modifying catalytically active metal centers. Therefore, the preparation of metal complexes of the less known 3-pyridyldiphenylphosphine is important. 3-Pyridyldiphenylphosphine could bridge two metal centers, but more importantly, it has different electronic properties as a ligand in comparison with the two other pyridyldiphenylphosphines.

Addition of 3-pyridyldiphenylphosphine to a tetrahydrofuran solution of Rh₂(μ-Cl)₂(CO)₄ produced a yellow solution from which a crystalline solid Rh(CO)Cl(3-PyPPh₂)₂ (**2**) was precipitated by addition of acetone. The 3-PyPPh₂ preferentially binds through the phosphorus atom to give the mononuclear complex. The crystal structure of **2** is very similar to the structures of the 2-PyPPh₂^{14,15} and PPh₃^{15–17} analogues. In the crystal structure of Rh(CO)Cl(3-PyPPh₂)₂ (**2**) (Fig. 1) the pyridylphosphine ligands are in *trans* positions. Rh^I has a square planar geometry and pseudomirror symmetry against the main position of the ring nitrogen atoms. The bond lengths of Rh–P (232.27 and 232.44 pm), Rh–C (180.8 pm) and Rh–Cl (236.88 pm) are in good agreement with the corresponding complex of PPh₃.¹⁷ A comparison of the spectroscopic parameters of Rh(CO)Cl(3-PyPPh₂)₂ (**2**) (³¹P 26.3 ppm, ¹J_{Rh–P} 117 Hz, ν_{CO} 1982 cm⁻¹) to the analogues¹⁵ of 2-PyPPh₂ (³¹P 30.1, ¹J_{Rh–P} 128 Hz, ν_{CO} 1982 cm⁻¹) and PPh₃ (³¹P 29.1 ppm, ¹J_{Rh–P} 124 Hz, ν_{CO} 1968 cm⁻¹) confirms the similar structure of **2** with the corresponding Rh^I complexes of 2-PyPPh₂ and PPh₃ also in solution.

The reaction of 3-pyridyldiphenylphosphine with Co₂(CO)₈ produced the disubstituted red-brown compound Co₂(CO)₆(3-PyPPh₂)₂. In the solid state the product was reasonably air-stable, whereas in solution the complex decomposed slowly. The IR spectra in the carbonyl region indicated an unbridged structure.¹⁸ No signals were found in the bridged carbonyl region around 1700 cm⁻¹. On comparing the IR parameters of Co₂(CO)₆(3-PyPPh₂)₂ (**3**) (2038, 1983, 1961 cm⁻¹) with those of the analogue of 2-pyridyldiphenylphosphine¹⁸

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (in pm^2).^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq) ^a
Rh	3289(1)	1494(1)	-24(1)	390(1)
Cl	3041(1)	513(1)	-481(1)	550(1)
P(1)	3407(1)	1262(1)	1865(1)	390(1)
P(2)	3224(1)	1671(1)	-1917(1)	400(1)
O(1)	3311(3)	2715(1)	482(3)	940(1)
C(1)	3332(3)	2246(1)	294(3)	540(1)
C(111)	3467(3)	1849(1)	2867(2)	450(1)
C(112)	2537(3)	1978(1)	3248(3)	570(1)
C(113)	2653(3)	2426(2)	4011(3)	710(1)
C(114)	3714(4)	2750(2)	4399(3)	710(1)
C(115)	4646(4)	2622(2)	4032(3)	790(1)
C(116)	4524(3)	2178(2)	3267(3)	710(1)
C(121)	2055(3)	852(1)	1788(2)	430(1)
C(122)	2114(3)	417(2)	2553(3)	740(1)
N(123)	1124(4)	105(2)	2479(4)	1130(1)
C(124)	13(4)	234(2)	1614(4)	830(1)
C(125)	-95(3)	651(2)	822(4)	790(1)
C(126)	941(3)	960(2)	920(3)	660(1)
C(131)	4740(2)	844(1)	2775(2)	450(1)
C(132)	5104(4)	818(2)	4000(3)	730(1)
C(133)	6094(4)	505(2)	4687(3)	790(1)
C(134)	6729(3)	208(2)	4182(3)	740(1)
C(135)	6418(3)	205(2)	2997(3)	630(1)
C(136)	5413(3)	527(1)	2283(3)	530(1)
C(211)	3007(2)	2407(1)	-2431(2)	420(1)
C(212)	1894(3)	2608(1)	-3227(3)	510(1)
C(213)	1758(3)	3167(2)	-3587(3)	640(1)
C(214)	2736(4)	3528(2)	-3167(3)	680(1)
C(215)	3850(3)	3344(1)	-2364(3)	640(1)
C(216)	3975(3)	2792(1)	-1998(3)	600(1)
C(221)	1947(3)	1315(1)	-3070(2)	460(1)
C(222)	2005(3)	1165(2)	-4137(3)	690(1)
N(223)	1032(4)	926(2)	-5017(3)	1050(1)
C(224)	-27(4)	839(2)	-4820(4)	960(2)
C(225)	-131(4)	989(2)	-3794(4)	960(2)
C(226)	859(3)	1226(2)	-2903(3)	770(1)
C(231)	4618(2)	1454(1)	-2138(2)	430(1)
C(232)	4996(3)	1704(2)	-2981(3)	590(1)
C(233)	6059(3)	1529(2)	-3114(3)	690(1)
C(234)	6748(3)	1105(2)	-2428(3)	720(1)
C(235)	6409(3)	847(2)	-1599(3)	660(1)
C(236)	5344(3)	1021(1)	-1451(3)	520(1)

^a*U*(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Table 3. Selected bond lengths (in pm) and angles (in °).

Atoms	Distances	Atoms	Angles
Rh-C(1)	180.8(3)	C(1)-Rh-P(2)	91.47(9)
Rh-P(2)	232.27(9)	C(1)-Rh-P(1)	91.76(9)
Rh-P(1)	232.44(9)	P(2)-Rh-P(1)	176.44(3)
Rh-Cl	236.88(10)	C(1)-Rh-Cl	174.93(10)
P(1)-C(131)	182.4(3)	P(2)-Rh-Cl	89.15(3)
P(1)-C(121)	182.2(3)	P(1)-Rh-Cl	87.76(3)
P(1)-C(111)	183.0(3)	C(131)-P(1)-Rh	116.72(9)
P(2)-C(231)	182.1(3)	C(121)-P(1)-Rh	110.32(9)
P(2)-C(221)	182.4(3)	C(111)-P(1)-Rh	117.32(9)
P(2)-C(211)	182.8(3)	C(231)-P(2)-Rh	113.65(9)
O(1)-C(1)	113.0(4)	C(221)-P(2)-Rh	113.37(10)
		C(211)-P(2)-Rh	117.43(9)
		O(1)-C(1)-Rh	177.3(3)

(2029, 1973, 1953 cm^{-1}), a shift of about 10 cm^{-1} was observed in every band. However, the similar structure of the IR spectra suggests similar symmetry in both of these complexes. Corresponding bands for PPh_3 ¹⁹ were 2022, 1977 and 1957 cm^{-1} .

Moderately weak hydroformylation activity was achieved with $\text{Rh}(\text{CO})\text{Cl}(\text{3-PyPPh}_2)_2$ (**2**). More significantly the double-bond migration became dominant, and large numbers of isomerization products were observed. The prepared Co complex (**3**) had no catalytic activity under relatively mild reaction conditions. Table 4 compares the product distributions obtained by $\text{Rh}(\text{CO})\text{Cl}(\text{3-PyPPh}_2)_2$, $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$.

Table 4. Hydroformylation of 1-hexene.

Metal complex	Aldehydes (%)	<i>i/n</i>	Isomerization (%)	Hydrogenation (%)
Rh ₄ (CO) ₁₂	35	1.3	41	13
Rh(NO ₃) ₃ · 2H ₂ O	32	1.2	45	14
Rh(CO)Cl(3-PyPPh ₂) ₂	14	1	73	2

$n(1\text{-hexene})/n(\text{Rh}) = 10\,000$, $t = 4\text{ h}$, $p(\text{CO}/\text{H}_2) = 20\text{ bar}$, $T = 100\text{ }^\circ\text{C}$.

Acknowledgement. Financial support from the Neste Foundation is gratefully acknowledged.

References

- Newkome, G. R. *Chem. Rev.* 93 (1993) 2067.
- Drent, E., Arnoldy, P. and Budzelaar, P. H. M. *J. Organomet. Chem.* 455 (1993) 247.
- Drent, E., Arnoldy, P. and Budzelaar, P. H. M. *J. Organomet. Chem.* 475 (1994) 57.
- Buhling, A., Kamer, P. C. J. and van Leeuwen, P. W. N. M. *J. Mol. Catal. A* 98 (1995) 69.
- Buhling, A., Kamer, P. C. J., van Leeuwen, P. W. N. M. and Elgersma, J. W. *J. Mol. Catal. A* 116 (1997) 297.
- Lazarowych, N. J., Morris, R. H. and Rossner, J. M. *Inorg. Chem.* 25 (1986) 3926.
- Mann, F. G. and Watson, J. *J. Org. Chem.* 13 (1948) 502.
- Newkome, G. R. and Hager, D. C. *J. Org. Chem.* 43 5 (1978) 947.
- Kurtev, K., Ribola, D., Jones, R. A., Cole-Hamilton, D. J. and Wilkinson, G. *J. Chem. Soc., Dalton Trans.* (1980) 55.
- Maisonnet, A., Farr, J. P., Olmstead, M. M., Hunt, C. T. and Balch, A. L. *Inorg. Chem.* 21 (1982) 3961.
- Bowen, R. J., Garner, A. C., Berners-Proce, S. J., Jenkins, I. D. and Sue, R. E. *J. Organomet. Chem.* 554 (1998) 181.
- Sheldrick, G. M. SHELXTL-Plus Release 4.11.v, Siemens Analytical X-Ray Instruments Inc., Madison, WI 1990.
- Sheldrick, G. M. SHELXL-93, University of Göttingen, Germany 1993.
- Farr, J. P., Olmstead, M. M. and Balch, A. L. *J. Am. Chem. Soc.* 102 (1980) 6654.
- Farr, J. P., Olmstead, M. M., Hunt, C. H. and Balch, A. L. *Inorg. Chem.* 20 (1981) 1182.
- Cerioti, A., Ciani, G. and Sironi, A. *J. Organomet. Chem.* 247 (1983) 345.
- Rheingold, A. L. and Geib, S. J. *Acta Crystallogr., Sect. C* 43 (1987) 784.
- Moreno, C., Macazaga, M. J. and Delgado, S. *Inorg. Chim. Acta* 182 (1991) 55.
- Manning, A. R. *J. Chem. Soc. A* (1968) 1135.

Received November 11, 1998.