$(Ph_3P)_2Rh(SPCy_2)$: A complex containing a side-on bonded η^2-secondary phosphine sulfide anion

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The reaction of $Cp_2Zr(SPCy_2)_2$ with either $(Ph_3P)_3RhH(CO)$ or $(Ph_3P)_4RhH$ led not to the expected heterobimetallic species but rather to a novel Rh species $(Ph_3P)_2Rh(SPCy_2)$, **4**. The $^{31}P\{^1H\}$ NMR spectrum of this complex is an ABCX pattern. The molecular geometry of **4** was confirmed by a crystallographic study. Compound **4** crystallizes in the space group $P2_1/c$ with $a = 10.912(1)$ Å, $b = 12.335(2)$ Å, $c = 32.346(7)$ Å, $\beta = 96.17(1)°$, $V = 4328(1)$ Å^3, and $Z = 4$. The coordination sphere about Rh in **4** is pseudo-square planar, containing three phosphorus and a sulfur atom from the two coordinated phosphines and a side-on bonded $SPCy_2$ moiety. This structural study confirms that the secondary phosphine chalcogenide is bonded to Rh in an η^2 fashion. The complex **4** is only the fourth example in which this mode of binding has been crystallographically confirmed and is the first such species to involve one of the Pt group metals.

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La réaction du $Cp_2Zr(SPCy_2)_2$ avec soit le $(Ph_3P)_3RhH(CO)$ ou le $(Ph_3P)_4RhH$ ne conduit pas aux espèces hétérobimétalliques attendues mais plutôt à une nouvelle espèce de Rh, le $(Ph_3P)_2Rh(SPCy_2)$, **4**. Le spectre rmn du $^{31}P\{^1H\}$ de ce complexe se présente sous la forme d'un arrangement ABCX. On a confirmé la géométrie moléculaire du composé **4** par une étude cristallographique. Le composé **4** cristallise dans le groupe d'espace $P2_1/c$ avec a = 10,912(1), b = 12,335(2) et c = 32,345(7) Å, β = 96,17(1)°, V = 4328(1) Å^3 et Z = 4. La sphère de coordination autour du Rh dans le composé **4** est pseudo plan carré et elle contient trois phosphores et un atome de soufre provenant de deux phosphines coordonnées et une portion de $SPCy_2$ liée sur le côté. Cette étude structurale permet de confirmer que la phosphine chalcogène secondaire est liée au Rh d'une façon η^2. Le complexe **4** n'est que le quatrième exemple dans lequel ce mode de liaison a pu être confirmé d'une façon cristallographique et il s'agit de la première espèce de ce type à incorporer un des métaux du groupe du Pt.

[Traduit par la revue]

Introduction

Our interest in early/late heterobimetallics (1–12) has led us to investigate the use of functionalized early transition metal complexes as metalloligands for later transition metals. In a recent paper we described syntheses, structures and chemistry of some Ti, Zr, and Hf complexes of secondary phosphine sulfides and selenides (9). In these Ti, Zr, and Hf complexes, bonding of XPR_2 anions through chalcogenide was observed. However, secondary phosphine chalcogenides or their conjugate bases are known to exhibit at least six different bonding modes (Fig. 1) (13–35). One of these modes involves bonding in which the chalcogen and phosphorus nuclei are bound to different metal atoms (Fig. 1(*e*)); however, this type of ligand system has not been employed to synthesize mixed metal species. Thus, the complex $Cp_2Zr(SPCy_2)_2$, **1**, seemed a suitable synthon for the preparation of Zr/M heterobimetallics. In this paper, we describe some initial investigations that show that reactions of **1** with two Rh-hydride species result in the cleavage of the Zr—S bond, yielding the monometallic species $(Ph_3P)_2Rh(SPCy_2)$, **4**. The species, **4**, has been characterized crystallographically. The results show that the secondary phosphine sulfide moiety is side-on bonded in an η^2 fashion. Although this form of binding is known, this report is only the fourth in which this form of bonding has been structurally confirmed.

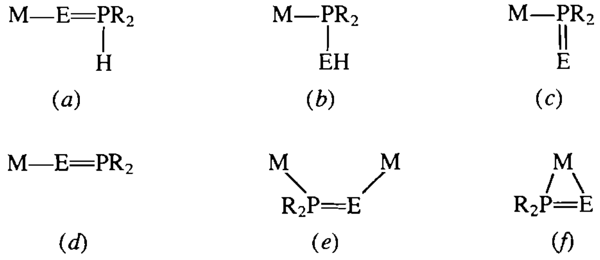

FIG. 1. Bonding modes of secondary phosphine chalcogenides.

Experimental section

All preparations were done under an atmosphere of dry, O_2-free N_2. Solvents were reagent grade, distilled from the appropriate drying agents under N_2, and degassed by the freeze–thaw method at least three times prior to use. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-200 spectrometer, using external 85% H_3PO_4 as the reference. The chemical shifts are reported in ppm relative to this reference. Melting points are reported uncorrected. The complex $Cp_2Zr(SPCy_2)_2$, **1**, $(Ph_3P)_3RhH(CO)$, **2**, and $(Ph_3P)_4RhH$, **3**, were prepared by published methods (9, 36).

Preparation of $(Ph_3P)_2Rh(SPCy_2)$, 4

To a benzene solution (5 mL) of 38 mg of **1** was added 50 mg of **2** in 5 mL of benzene. The solution was stirred for 12 h. The product precipitated from solution upon addition of hexane. The orange–red crystalline material was recrystallized from benzene/hexane. Replacement of **2** with an equivalent of **3** also affords the isolation of **4** via an identical work up procedure. Yield 35 mg (75%). ^1H NMR (δ, C_6D_6): 7.1–7.4 (m, 30 H), 2.2–2.8 (m, 22 H). $^{31}P\{^1H\}$ NMR (C_6H_6, δ, J (Hz)): 40.80 (P3, d of d of d, 1P), 48.20 (P2, d of d of d, 1P), 87.38 (P1, d of d of d, 1P), $|J_{P1—Rh}| = 87.9$, $|J_{P2—Rh}| = 215.6$, $|J_{P3—Rh}| = 168.7$, $|J_{P1—P2}| = 28.4$, $|J_{P1—P3}| = 231.6$, $|J_{P2—P3}| = 30.1$.

X-ray data collection and reduction

Orange–red crystals of **1** were obtained by vapour diffusion of hexane into a benzene solution of **2**. Diffraction experiments were performed on a four-circle Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrix was obtained from 15 machine-centred reflections selected from a rotation photograph. These data were used to determine the crystal system. Partial rotation photographs around each axis were consistent with a monoclinic crystal system. Ultimately, 37 reflections (4.7° < 2θ <

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TABLE 1. Crystallographic parameters

Formula	$C_{48}H_{52}P_3SRh$
Crystal colour, form	Orange–red blocks
a (Å)	10.912(1)
b (Å)	12.335(2)
c (Å)	32.346(7)
β (deg)	96.17(1)
Crystal system	Monoclinic
Space group	$P2_1/c$
Volume (Å^3)	4328(1)
Density (g cm^{-3})	1.31
Z	4
Crystal dimensions (mm)	0.40 × 0.30 × 0.40
Absorption coefficient, μ (cm^{-1})	5.10
Radiation λ, (Å)	Mo Kα (0.71069)
Temperature (°C)	24
Scan speed (deg/min)	2.0–5.0 ($\theta/2\theta$ scan)
Scan range (deg)	1.0 below Kα_1 1.0 below Kα_2
Background/scan time ratio	0.5
Data collected	3002
No. of unique data $F_o^2 > 3\sigma(F_o^2)$	2088
No. of variables	166
R (%)	4.53
R_w (%)	5.32
Largest Δ/σ in the final least squares cycle	0.001
Maximum residual electron density (e/Å^3) (atom associated)	0.49 (C84—C85)

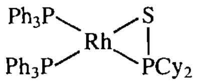
25°) were used to obtain the final lattice parameters and the orientation matrix. Machine parameters, crystal data, and data collection parameters are summarized in Table 1. The observed extinctions were consistent with the space group $P2_1/c$. All $\pm h$, $+k$, $+l$ data were collected in one shell ($4.5° < 2\theta < 35.0°$) and three standard reflections were recorded every 197 reflections. Their intensities showed no statistically significant change over the duration of the data collection. The data were processed using the SHELX-76 program package on the computing facilities at the University of Windsor. A total of 3002 reflections with $F_o^2 > 3\sigma F_o^2$ were used in the refinement. The absorption coefficient was small (μ = 5.10 5.10 cm^{-1}) and thus no absorption correction was applied to the data.

Structure solution and refinement

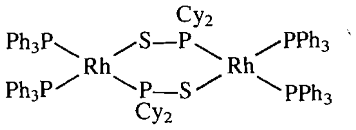
Non-hydrogen atomic scattering factors were taken from the literature tabulations (37–39). The Rh atom position was determined using the heavy atom (Patterson) method. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The initial refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ where the weight, w, is defined as $4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of refinement the Rh, P and S atoms were assigned anisotropic temperature factors. The carbon atoms of the phenyl and cyclohexyl rings were described by isotropic thermal parameters. The phenyl ring geometries were constrained to that of a hexagon with a carbon–carbon distance of 1.39 Å. Hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C—H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. In all cases the hydrogen atom contributions were calculated, but not refined. The final values of R and R_w are given in Table 1. The maximum Δ/σ on any of the parameters in the final cycles of the refinement and the location of the largest peaks in the final difference Fourier map calculation are also given in Table 1. The residual electron densities were of no chemical significance. The following data are tabulated: positional parameters (Table 2) and selected bond distances and angles (Table 3). Thermal parameters (Table S1), hydrogen atom parameters (Table S2), bond distances and angles associated with the cyclohexyl rings (Table S3) and values of $10|F_o|$ and $10|F_c|$ (Table S4) have been deposited as supplementary material.[3]

Results and discussion

The reaction of **1** with either $(Ph_3P)_3RhH(CO)$ or $(Ph_3P)_4RhH$ resulted in the immediate formation of an orange–red product, **4**. This material exhibits a ^{1}H NMR spectrum that shows only phenyl and cyclohexyl proton resonances, indicating the loss of the Cp_2Zr fragment. The $^{31}P\{^1H\}$ NMR spectrum contains three distinct resonances each comprised of a doublet of doublets of doublets. This ABCX spectrum (Fig. 2) is consistent with three inequivalent phosphorus nuclei about a pseudo-square planar Rh atom. The resonances were assigned to P1 (the phosphorus of the $SPCy_2$ moiety), P2 (the phosphorus of the PPh_3 *cis* to P1) and P3 (the phosphorus of the PPh_3 *trans* to P1) on the basis of chemical shifts and coupling constants. The expectation of square planar coordination geometry for Rh suggests that the S of the $SPCy_2$ moiety is also bound to Rh. This is consistent with either a monometallic species containing an η^2 bound secondary phosphine sulfide, **4**, a dimeric, **5**, or an oligomeric complex. The magnitude of the P1—Rh coupling constant suggests the incorporation of P1 in a three-membered ring, thus suggesting a monometallic species (15, 29). Such η^2 binding of SPR_2 moieties to Rh has been previously postulated on the basis of spectroscopic data (17, 29) and is herein confirmed by X-ray crystallography (*vide infra*). This mode of binding of a secondary phosphine sulfide has also been confirmed for Mo (15, 35) and Fe (34) complexes. Complexes in which SPR_2 moieties are bound in a η^2 fashion have been postulated as intermediates in a number of reactions and are generally considered to be unstable (19–21, 26, 27, 34).



4



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The mechanism of formation of **4** is not known nor is the nature of the Zr-containing product. It is clear, however, that cleavage of a Zr—S bond must occur in the process of the formation of **4**. Such lability of Zr—S bonds has been noted in other Zr—S chemistry (9).

Structure description

The crystallographic investigation of **4** revealed that the unit cell is monoclinic with a single discrete molecule in the asymmetric unit. The closest non-bonded distance between discrete molecules is 2.380 Å (H15B---H73). An ORTEP drawing of the molecule is shown in Fig. 3. The coordination sphere of Rh is pseudo-square planar containing three phos-

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[3] A complete set of data, including thermal parameters (Table S1), hydrogen atom parameters (Table S2), and bond distances and angles associated with the cyclohexyl rings (Table S3) (6 pages); values of $10|F_o|$ and $10|F_c|$ (Table S4) (8 pages), may be purchased from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

TABLE 2. Positional parameters[a]

Atom	x	y	z	Atom	x	y	z
Rh	3592(1)	1398(1)	3778(1)	S	4826(2)	1353(2)	4438(1)
P1	4325(2)	−56(2)	4143(1)	P2	2309(2)	826(2)	3243(1)
P3	3394(2)	3244(2)	3750(1)	C11	5705(8)	−809(8)	4037(3)
C12	6485(9)	−145(8)	3761(3)	C13	7650(9)	−739(9)	3668(3)
C14	8411(10)	−1075(9)	4074(3)	C15	7659(10)	−1772(9)	4339(4)
C16	6491(9)	−1194(8)	4432(3)	C21	3494(8)	−924(7)	4480(3)
C22	3283(9)	−2079(8)	4308(3)	C23	2684(9)	−2803(8)	4618(3)
C24	1454(9)	−2312(8)	4711(3)	C25	1599(10)	−1125(9)	4860(4)
C26	2247(9)	−446(8)	4555(3)	C31	2626(6)	1009(5)	2697(2)
C32	3469(6)	1800(5)	2604(2)	C33	3703(6)	1967(5)	2193(2)
C34	3093(6)	1343(5)	1875(2)	C35	2250(6)	553(5)	1968(2)
C36	2017(6)	386(5)	2378(2)	C41	743(6)	1383(5)	3250(2)
C42	338(6)	1501(5)	3642(2)	C43	−799(6)	1984(5)	3682(2)
C44	1532(6)	2348(5)	3329(2)	C45	1128(6)	2229(5)	2937(2)
C46	10(6)	1747(5)	2897(2)	C51	2032(5)	−655(5)	3231(2)
C52	3026(5)	−1322(5)	3166(2)	C53	2869(5)	−2444(5)	3144(2)
C54	1719(5)	−2898(5)	3187(2)	C55	726(5)	−2231(5)	3252(2)
C56	882(5)	−1109(5)	3274(2)	C61	4740(5)	3955(6)	4011(2)
C62	4602(5)	4880(6)	4250(2)	C63	5640(5)	5406(6)	4444(2)
C64	6815(5)	5008(6)	4400(2)	C65	6953(5)	4083(6)	4161(2)
C66	5916(5)	3556(6)	3967(2)	C71	2152(6)	3746(5)	4040(2)
C72	1954(6)	3158(5)	4395(2)	C73	1013(6)	3462(5)	4631(2)
C74	271(6)	4353(5)	4512(2)	C75	469(6)	4941(5)	4157(2)
C76	1410(6)	4637(5)	3921(2)	C81	3137(5)	3967(5)	3251(2)
C82	1981(5)	3919(5)	3021(2)	C83	1813(5)	4359(5)	2622(2)
C84	2799(5)	4847(5)	2453(2)	C85	3954(5)	4895(5)	2683(2)
C86	4123(5)	4455(5)	3083(2)				

[a] Multiplied by 10^4.

TABLE 3. Selected bond distances (Å) and angles (deg)

Bond	Distance	Bond	Distance	Bond	Distance
Rh—P1	2.248(3)	Rh—P2	2.219(3)	Rh—P3	2.287(3)
Rh—S	2.399(3)	P1—S	2.028(4)	P1—C11	1.833(9)
P1—C21	1.836(9)	P2—C31	1.853(7)	P2—C41	1.844(7)
P2—C51	1.854(7)	P3—C61	1.838(8)	P3—C71	1.837(7)
P3—C81	1.837(7)				

Bonds	Angle	Bonds	Angle	Bonds	Angle
S—Rh—P1	51.6(1)	S—Rh—P2	158.8(1)	P1—Rh—P2	108.4(1)
S—Rh—P3	95.8(1)	P1—Rh—P3	147.3(1)	P2—Rh—P3	103.6(1)
Rh—S—P1	60.3(1)	Rh—P1—S	68.0(1)	C11—P1—C21	106.5(4)
C31—P2—C41	103.6(3)	C31—P2—C51	98.4(3)	C41—P2—C51	102.5(3)
C61—P3—C71	101.6(3)	C61—P3—C81	102.2(3)	C71—P3—C81	103.5(3)

phorus atoms and a sulfur atom. The Rh—P1 bond distance is 2.248(3) Å. In comparison, the Rh—P bonds involving the PPh_3 moieties are 2.219(3) and 2.287(3) Å. All of these Rh—P distances are typical of those seen in other Rh–phosphine complexes (39). The Rh—P3 distance is longer than the Rh—P2 distance reflecting the *trans* influence of the basic phosphorus atom of the $SPCy_2$ moiety. The Rh—S bond distance of 2.399(3) Å is slightly longer than the Rh—S distance found in $[Rh(MeSCH_2CH_2PPh_2)_2]BF_4$ (2.353(3) and 2.342(3) Å) (40). Poorer donor ability of the sulfur of a $SPCy_2$ anion compared to that of the thioether sulfur of $MeSCH_2CH_2PPh_2$ may arise from the presence of P—S multiple bonding. In addition, the strain associated with the three-membered ring may result in poor orbital overlap between S and Rh.

The P1—Rh—P2 and P3—Rh—S angles of 108.4(1) and 95.8(1)° are consistent with the pseudo-square planar geometry about Rh. The P2—Rh—P3 angle of 103.6(1)° compares with the angle of 92.9(1)° found between the phosphine groups in $[Rh(COD)(PPh_2(C_4H_4S))_2]^+$ (40). Steric interactions between the phenyl rings on P2 with the cyclohexyl groups on P1 are apparently minimized by the orientation of the rings, such that only ring 5 (C51—C56) is directed towards the cyclohexyl groups. Steric interactions with the phenyl rings on P2 with

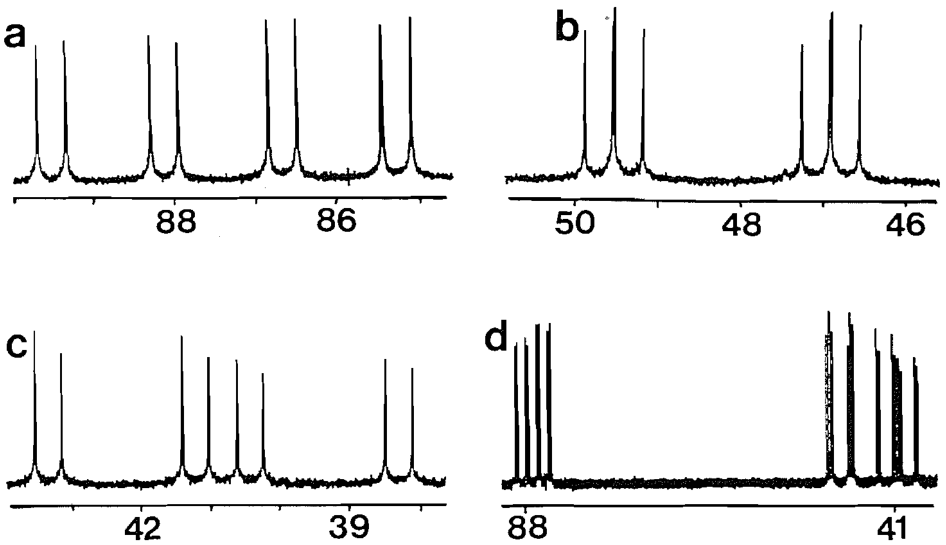

FIG. 2. $^{31}P\{^1H\}$ NMR Spectrum of **4**, scales are given in ppm. Expansion of the signals arising from P1, P2, and P3 are shown in (*a*), (*b*), and (*c*) respectively; (*d*) full spectrum.

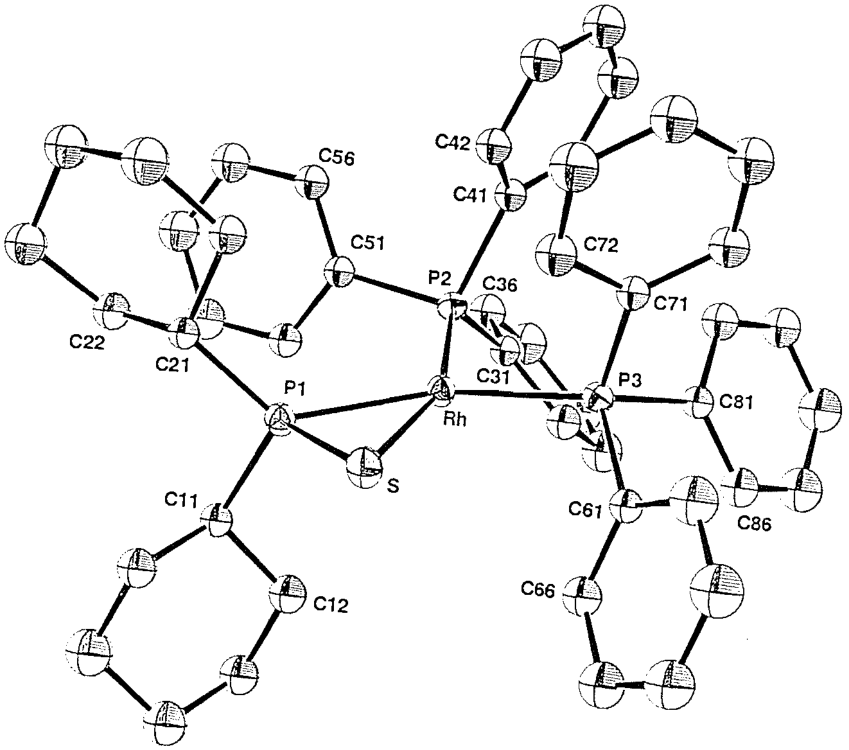

FIG. 3. ORTEP drawing of **4**, hydrogen atoms are omitted for clarity, 30% thermal ellipsoids are shown.

those on P3 are relived by the relatively large P2—Rh—P3 angle. These steric constraints are also reflected in the fact that the S—Rh—P3 angle (95.8(1)°) is smaller than the P1—Rh—P2 angle (108.4(1)°). The P1—Rh—S angle is 51.6(1)°. This is similar to the P—Fe—S angle of 51.13(3)° found in $(C_3F_7)Fe(CO)_3(SPEt_2)$, **6**, (34) and in contrast to the P—Mo—S angles of 47.11(5) and 46.91(5)° found in $Mo(CO)_2(PPh_3)(SPPh_2)_2$, **7** (15) and 47.5(1)° found in $(MeC_5H_4)Mo(CO)_2(\eta^2\text{-}SPPh_2)$, **8** (35). The larger angle at the metal center in **4** is consistent with the shorter M—P and M—S distances.

The P1—S bond distance of 2.028(4) Å is considerably longer than the typical P—S double bond length of 1.95 Å and shorter than P—S single bond lengths of 2.18 Å (15). The observed P—S distance in **4** is comparable to the P—S bond distances in the complexes containing η^2-bound SPR_2 units **6** (2.011(1) Å) (34), **7** (2.008(2), 2.013(2) Å) (15), and **8** (2.003(2) Å) (35). Thus, the P—S bond distance reflects a considerable degree of π bonding between phosphorus and sulfur.

Summary

The reaction of **1** with two Rh hydrides does not lead to the formation of stable heterobimetallics. Rather, the monometallic species **4** is formed. The structural study described herein, confirms the η^2 bonding mode of the secondary phosphine sulfide anion. The complex **4** is only the fourth example in which this mode of binding has been crystallographically confirmed and is the first such species to involve one of the Pt group metals.

Acknowledgements

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1. L. Gelmini, L. C. Matassa, and D. W. Stephan. Inorg. Chem. **24**, 2585 (1985).
2. L. Gelmini and D. W. Stephan. Inorg. Chem. **25**, 1222 (1986).
3. L. Gelmini and D. W. Stephan. Inorg. Chim. Acta, **111**, L17 (1986).
4. S. J. Loeb, H.-A. Taylor, L. Gelmini, and D. W. Stephan. Inorg. Chem. **25**, 1977 (1986).
5. G. S. White and D. W. Stephan. Inorg. Chem. **24**, 1499 (1985).
6. T. A. Wark and D. W. Stephan. Inorg. Chem. **26**, 363 (1987).
7. G. S. White and D. W. Stephan. Organometallics, **6**, 2169 (1987).
8. T. A. Wark, G. S. White, J. S. Tse, and D. W. Stephan. Unpublished results.
9. L. Gelmini and D. W. Stephan. Organometallics, **6**, 1515 (1987).
10. G. S. White and D. W. Stephan. Organometallics. **7**, 903 (1988).
11. L. Gelmini and D. W. Stephan. Organometallics. **7**, 849 (1988).
12. W. Zheng and D. W. Stephan. Inorg. Chem. **27**, 2386 (1988).
13. O. J. Scherer, H. Jungmann, C. Kruger, and G. Wolmerschauser. Chem. Ber. **117**, 2382 (1984).
14. E. Lindner, F. Bouachir, and S. Hoehne. Chem. Ber. **116**, 45 (1983).
15. H. P. M. Ambrosius, J. H. Noordik, and G. J. A. Ariaans. J. Chem. Soc. Chem. Commun. 832 (1980).
16. W. Malisch, R. Maisch, I. J. Colquhoun, and W. McFarlane. J. Organomet. Chem. **220**, C4 (1981).
17. V. Marsala, F. Faraone, and P. Piraino. J. Organomet. Chem. **133**, 301 (1977).
18. E. Lindner, F. Bouachir, and W. Hiller. J. Organomet. Chem. **210**, C37 (1981).
19. E. Lindner, A. Rau, and S. Hoehne. Angew. Chem. Int. Ed. Engl. **20**, 787 (1981).
20. E. Lindner, A. Rau, and S. Hoehne. Chem. Ber. **114**, 3281 (1981).
21. E. Lindner and W. P. Meier. J. Organomet. Chem. **114**, 67 (1976).
22. G. J. Kruger, S. Lotz, L. Linford, M. Van Dyk, and H. G. Raubenheimer. J. Organomet. Chem. **280**, 241 (1985).
23. E. Lindner and C. P. Krieg. J. Organomet. Chem. **269**, 65 (1984).
24. W. Klaui, K. Schmidt, A. Bockman, P. Hofmann, H. R. Schmidt, and P. Stauffert. J. Organomet. Chem. **286**, 407 (1985).
25. E. Lindner, K. Auch, W. Hiller, and R. Fawzi. Angew. Chem. Int. Ed. Engl. **23**, 320 (1984).
26. E. Lindner, C. P. Krieg, W. Hiller, and R. Fawzi. Chem. Ber. **118**, 1398 (1985).
27. E. Lindner, C. P. Krieg, W. Hiller, and D. Hubner. Chem. Ber. **117**, 489 (1984).
28. B. Walther, B. Messbauer, and H. Meyer. Inorg. Chim. Acta, **37**, L525 (1979).
29. D. H. M. W. Thewissen. J. Organomet. Chem. **192**, 115 (1980).
30. K. P. Wagner, R. W. Hess, P. M. Triechel, and J. C. Calabrese. Inorg. Chem. **14**, 1121 (1975).
31. B. Messbauer, H. Meyer, B. Walther, M. J. Heeg, A. F. M. M. Rahman, and J. P. Oliver. Inorg. Chem. **22**, 272 (1983).
32. B. Walther. Coord. Chem. Rev. **60**, 67 (1984).
33. J. R. Wasson, G. M. Woltermann, and H. J. Stoklosa. Top. Curr. Chem. **35**, 65 (1973).
34. E. Lindner, C. P. Krieg, W. Hiller, and R. Fawzi. Angew. Chem. Int. Ed. Engl. **23**, 523 (1984).
35. H. Alper, F. W. B. Einstein, F. W. Hartstock, and R. H. Jones. Organometallics, **6**, 829 (1987).
36. G. Wilkinson. Inorg. Synth. **13**, 126 (1972).
37. D. T. Cromer and J. B. Mann. Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. A**24**, 324 (1968).
38. D. T. Cromer and J. B. Mann. Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. A**24**, 390 (1968).
39. D. T. Cromer and J. T. Waber. International tables for X-ray crystallography. Kynoch Press, Birmingham, England. 1974.
40. D. G. Dick and D. W. Stephan. Can. J. Chem. **64**, 1870 (1986).