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Complexes of distibinomethane ligands
3. Manganese and rhenium carbonyl complexes[☆]

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Abstract

Photolysis of $Mn_2(CO)_{10}$ with the distibinomethanes $Ph_2SbCH_2SbPh_2$ (dpsm) and $Me_2SbCH_2SbMe_2$ (dmsm) yields $[Mn_2(CO)_6(dpsm)_2]$ and $[Mn_2(CO)_8(dmsm)]$, respectively, which have been characterised by IR, ^1H, $^{13}C\{^1H\}$ NMR spectroscopies and fast atom bombardment (FAB) mass spectrometry. Similar photolysis of the ligands with $Re_2(CO)_{10}$ yields axially substituted $[Re_2(CO)_9(\eta^1\text{-distibinomethane})]$. The X-ray crystal structure of $[Mn_2(CO)_6(dpsm)_2]$ reveals two dpsm ligands, each bonding to the two metal centres [Mn–Mn 3.098(2), Mn–Sb 2.487(2)–2.500(2) Å].

Keywords: Manganese; Rhenium; Distibine; NMR

1. Introduction

Diphosphinomethanes ($R_2PCH_2PR_2$, R=Me, Ph, Cy, etc.) have a rich coordination chemistry, which has been studied in great detail [1]. In contrast, although distibinomethanes $R_2SbCH_2SbR_2$ [R=Me (dmsm) or Ph (dpsm)] were first reported in the 1970s, their coordination chemistry has received little study [2]. In recent work [3,4], we have described complexes with Cr, Mo, W, Fe, Co, Ni and Mn carbonyls and some carbonyl halides, and identified three coordination modes, i.e., monodentate, bridging bidentate, and bridging across M–M bonds, but significantly, no examples of chelation. Neither distibinomethane reacted thermally with $Mn_2(CO)_{10}$, but moderate yields of $[Mn_2(CO)_8(L\text{–}L)]$ (L–L=dmsm or dpsm) (I see Fig. 1) were obtained using $\{[CpFe(CO)_2]_2\}$ as a catalyst [4]. No reaction occurred with $Re_2(CO)_{10}$ under similar conditions [4]. Subsequently, we established that photolysis of mixtures of $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ with $SbPh_3$ in toluene was a more facile route and led to higher degrees of substitution than either catalytic routes or the use of Me_3NO [5]. We therefore re-examined the reactions of the two decacarbonyls with the distibinomethanes using photolysis, and report the results here.

2. Experimental

Physical measurements were made as described previously [3–5].

2.1. $[Mn_2(CO)_6(dpsm)_2]$

$Mn_2(CO)_{10}$ (0.4 g, 1.0 mmol) and dpsm (0.56 g, 1.0 mmol) in toluene (40 ml) were irradiated under nitrogen with stirring for 17 h in an attempt to produce $[Mn_2(CO)_8(dpsm)]$. The mixture was then adsorbed onto alumina and eluted with dichloromethane to give $Mn_2(CO)_{10}$ (first band — yellow) and $[Mn_2(CO)_6(dpsm)_2]$ (second band — yellow). The solvent was removed from the collected fractions and the residue was recrystallised from dichloromethane–ethanol to give an orange solid. This was filtered, washed with ethanol (2×10 ml) and dried in vacuo. Yield: 0.14 g (10%). Found: C, 48.0; H, 3.3. Calc. for $C_{56}H_{44}Mn_2O_6Sb_4$: C, 47.7; H, 3.1%. ^1H NMR ($CDCl_3$): 3.2, 7.2–7.6. ^{55}Mn NMR ($CDCl_3/CH_2Cl_2$): −1945, $W_{1/2}$ 15 000 Hz. MS (FAB): 1273,

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[☆] Part 2 is Ref. [3].

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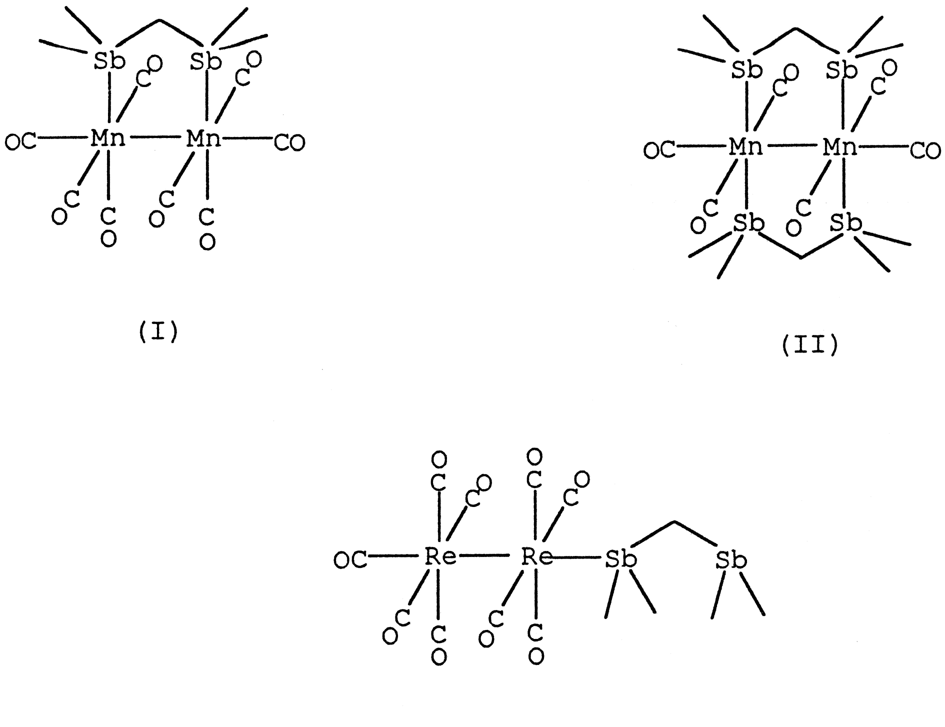

(I)

(II)

(III)

Fig. 1. Schematic diagram of the types of structure.

1117, 788. Calc. for $[C_{51}H_{44}Mn_2O_6^{121}Sb_4]^+$ 1266, $[C_{43}H_{32}Mn_2O_6^{121}Sb_3]^+$ 1117, $[C_{29}H_{22}Mn_2O_4^{121}Sb_2]^+$ 786.

2.2. [$Mn_2(CO)_8$(dmsm)]

$Mn_2(CO)_{10}$ (0.22 g, 0.56 mmol) and dmsm (0.36 g, 1.14 mmol) in toluene (40 ml) were irradiated under nitrogen with stirring for 17 h in an attempt to produce [$Mn_2(CO)_6(dmsm)_2$]. The mixture was then adsorbed onto alumina and eluted with hexane followed by dichloromethane–hexane (1:3, v/v) to give $Mn_2(CO)_{10}$ (first band — yellow) and [$Mn_2(CO)_8$(dmsm)] (second band — yellow). The solvent was removed from the collected fractions and dried in vacuo to give a yellow solid. Yield: 0.07 g (19%). The compound was identified by comparison of its spectroscopic properties with those reported previously [4].

2.3. [$Re_2(CO)_9$(dpsm)]

$Re_2(CO)_{10}$ (0.50 g, 0.77 mmol) and dpsm (0.44 g, 0.77 mmol) in toluene (40 ml) were irradiated under nitrogen with stirring for 17 h. The mixture was then adsorbed onto alumina and eluted with hexane followed by dichloromethane to give $Re_2(CO)_{10}$ (first band — colourless) and [$Re_2(CO)_9$(dpsm)] (second band — yellow). The solvent was removed from the collected fractions and the residue was recrystallised from dichloromethane–hexane to give a yellow solid. This was filtered, washed with hexane (2×10 ml) and dried in vacuo. Yield: 0.15 g (16%). Found: C, 33.9; H, 2.1. Calc. for $C_{34}H_{22}O_9Re_2Sb_2$: C, 34.4; H, 1.9%. ^{1}H NMR ($CDCl_3$): 3.3, 7.1–7.5. MS (FAB): 1162, 597. Calc. for $[C_{33}H_{22}O_8^{187}Re_2^{121}Sb_2]^+$ 1162, $[C_8O_8^{187}Re_2]^+$ 598.

2.4. [$Re_2(CO)_9$(dmsm)]

$Re_2(CO)_{10}$ (0.30 g, 0.46 mmol) and dmsm (0.15 g, 0.46 mmol) in toluene (40 ml) were irradiated under nitrogen with stirring for 17 h. The mixture was then adsorbed onto alumina and eluted with hexane followed by dichloromethane–hexane (1:2, v/v) to give $Re_2(CO)_{10}$ (first band — colourless) and [$Re_2(CO)_9$(dmsm)] (second band — yellow). The solvent was removed from the collected fractions and the residue was recrystallised from dichloromethane–hexane under nitrogen to give a yellow solid. This was filtered, washed with hexane (2×10 ml) and dried in vacuo. Yield: 0.25 g (58%). Found: C, 17.4; H, 1.2. Calc. for $C_{14}H_{14}O_9Re_2Sb_2$: C, 17.8; H, 1.5%. ^{1}H NMR ($CDCl_3$): 1.6, 2.2.

2.5. Crystal structure determination

Tiny orange crystals of [$Mn_2(CO)_6(dpsm)_2$] were obtained from a dichloromethane solution by layering with ethanol. Attempts to obtain larger crystals were not successful and a crystal (0.025×0.025×0.050 mm) was mounted on a Nonius CCD area detector diffractometer using the oil-film mounting technique and held at 150 K.

2.5.1. Crystal data

_$C_{56}H_{44}Mn_2O_6Sb_4$, $M_r = 1409.79$, triclinic, space group P1 (no. 2), $a = 11.980(2)$, $b = 12.726(2)$, $c = 19.627(4)$ Å, $\alpha = 72.15(1)$, $\beta = 74.49(1)$, $\gamma = 66.61(1)°$, $V = 2577.5(8)$ Å^3, $Z = 2$, $D_{calc} = 1.817$ g cm^{-3}, $T = 150(2)$ K, μ(Mo–K$_\alpha$) = 25.91 cm^{-1}, $F(000) = 1364$.

2.5.2. Data collection, solution and refinement

Using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å), 32 334 reflections were recorded using ψ- and ω-scans and gave, after data-processing, 8351 unique reflections (2θ(max) = 50.0°). An empirical absorption correction (sortav [6]) was applied, together with the Lorentz and polarization effects. The structure was solved by direct methods [7] to locate the heavy atoms and many of the C and O atoms, and the remaining atoms were located using structure factor and electron density calculations. No convincing hydrogen atoms were identified in later electron density maps, and H atoms were not included in the model. Full-matrix least-squares refinement [8] on F^2 using all of the data and 613 parameters (all atoms anisotropic) converged to $R1 = 0.066$ ($F > 4\sigma(F)$, 4817 reflections), w$R2$ (all data) = 0.183. $R1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$, $wR2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w F_0^4]^{1/2}$. The residual electron density was in the range −0.97 to +1.21 e Å^{-3} and with the peaks close to the heavy atoms.

3. Results and discussion

3.1. Complexes derived from $Mn_2(CO)_{10}$

Photolysis (370 nm) of a mixture of $Mn_2(CO)_{10}$ and dpsm (mol ratio, 1:1) in toluene gave an orange solution and some black decomposition products. Evaporation of the orange solution, followed by chromatography on alumina (CH_2Cl_2), produced an orange solid that was identified as $[Mn_2(CO)_6(dpsm)_2]$ (II). Curiously, the 1:1 complex $[Mn_2(CO)_8(dpsm)]$ [4] was not produced in significant amounts. The high level of substitution of CO groups in this complex is unusual for distibinomethanes, which often fail to displace more than one carbonyl group from a metal centre [4]. In surprising contrast, the use of a 1:2 mol ratio of $Mn_2(CO)_{10}$–dmsm under otherwise identical conditions gave $[Mn_2(CO)_8(dmsm)]$. Further photolysis of $[Mn_2(CO)_8(dmsm)]$ and dmsm in toluene resulted in extensive decomposition to black solids, and IR spectroscopic studies of the residual solution did not show any evidence of $[Mn_2(CO)_6(dmsm)_2]$. The spectroscopic properties of $[Mn_2(CO)_8(dmsm)]$ have been described previously (see also Table 1) [4]. The identification of $[Mn_2(CO)_6(dpsm)_2]$ as having structure (II) follows from the IR spectrum (Table 1), which exhibits a similar pattern of ν(CO) bands to $[Mn_2(CO)_6(diphosphine)_2]$ [9,10], although, due to the lower basicity of dpsm, the frequencies are considerably higher than in the diphosphine complexes. The structure was confirmed by an X-ray crystal structure determination. No evidence for the formation of a distibine analogue of $[Mn_2(CO)_5(diphosphine)_2]$, which contains four terminal- and one semi-bridging carbonyl groups was found.

3.2. Crystal structure of $[Mn_2(CO)_6(dpsm)_2]$

Tiny orange crystals of $[Mn_2(CO)_6(dpsm)_2]$ were obtained from a dichloromethane solution by layering with ethanol; attempts to obtain larger crystals were not successful. The structure consists of discrete molecules based on $Mn_2(CO)_{10}$, with the substitution of two distibine ligands for four CO groups. The distibine bridges the two Mn atoms and is shown in Fig. 2 with geometry details given in Table 2. The distibine ligand shows changes in geometry from that of the uncomplexed ligand [4], thus the Sb–C–Sb angle becomes smaller [103.0(5), 106.7(5)° compared with 117.3(2)°] and the C–Sb–C angles become larger [97.4(4)–104.0(5), av. 100.5(2.2)° compared with 94.4(1)–98.7(1), av. 96.7°]. The Mn–Mn bond [3.098(2) Å] is longer than in the parent carbonyl [11] [2.8950(6) Å] and the ('equatorial') CO groups show the displacement towards the non-bonded Mn atom. The torsion angles about the Mn–Mn bond (ca. 30°, see Table 2) are smaller than in the parent, presumably due to the steric requirements of the bridging distibine, but they still show a markedly staggered arrangement. Related compounds whose structures have been reported include the diarsine complex [12] $[Mn_2(CO)_8(Ph_2AsCH_2AsPh_2)]$ [Mn–Mn 2.962(2), Mn–As 2.411(3), 2.407(2) Å] and a diphosphine where substitution by both one and two ligands is reported [9] $[Mn_2(CO)_{10-2n}(R_2PCH_2PR_2)_n]$ ($n = 1, 2$; $R = C_6H_{11}$).

Table 1
Selected spectroscopic data

Complex	ν(CO)/cm^{-1} (CH_2Cl_2 solution)	ν(CO)/cm^{-1} (Nujol mull)	$^{13}C\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$)
$[Mn_2(CO)_6(dpsm)_2]$	1998(w),1969(w),1917(m),1903(s)	1976(br),1916(s),1898(s)	22.4(CH_2), 127–138(Ph), 223.7, 226.4(CO)
$[Mn_2(CO)_8(dmsm)]$[a]	2047(s),1983(s),1962(s),1929(m),1910(m)	–	–
$[Re_2(CO)_9(dpsm)]$	2086(w),2006(sh),1996(s),1974(s),1940(m)	2084(w),2004(sh),1994(s),1965(s),1927(s)	0.5(CH_2), 129–136(Ph), 186–199(CO)
$[Re_2(CO)_9(Ph_3Sb)]$[b]	2086(w),2009(sh),1996(s),1971(s),1925(m)[b]	2082(m),2008(sh),1994(s),1978(s),1925(s)	–
$[Re_2(CO)_9(dmsm)]$	2080(w),2005(sh),1994(s),1970(s),1940(m)	2080(m),2004(sh),1983(s,br),1925(sh)	−6.0, −1.6 (Me), −0.5(CH_2), 188–198(CO)

[a] Compare ν(CO)/cm^{-1} (CH_2Cl_2) from Ref. [4]. 2047(s), 1983(s), 1961(s), 1931(m), 1912(m).

[b] Data are from Ref. [5].

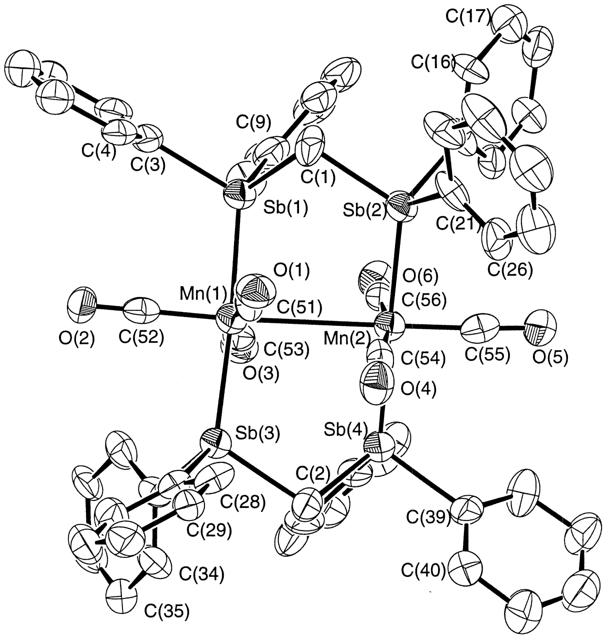

Fig. 2. Structure of [$Mn_2(CO)_6(Ph_2SbCH_2SbPh_2)_2$] showing the atom labelling scheme. The ellipsoids are drawn at the 50% probability level.

3.3. Complexes derived from $Re_2(CO)_{10}$

Photolysis of $Re_2(CO)_{10}$ and dpsm (1:1 ratio) in toluene gave yellow [$Re_2(CO)_9$(dpsm)] as the only significant product. This parallels the result obtained with Ph_3Sb, where ax-[$Re_2(CO)_9(Ph_3Sb)$] was the only photo-product from $Re_2(CO)_{10}$ and Ph_3Sb [5]. [$Re_2(CO)_9$(dpsm)] is poorly soluble in organic solvents and attempts to obtain a crystal for an X-ray study have failed. However, the identification of the isomer present as the axially substituted one (III) follows from the very similar pattern of ν(CO) to that observed in ax-[$Re_2(CO)_9(Ph_3Sb)$] (Table 1). The formulation is also consistent with the small shifts in $\delta(CH_2)$ in both the ^{1}H and ^{13}C{^{1}H} NMR spectra on coordination, which contrast with the large high frequency shifts observed when the dpsm is part of a five-membered metallocyclic ring, as in [$Mn_2(CO)_8$(dpsm)] or [$Mn_2(CO)_6(dpsm)_2$]. As noted before [5], the ^{13}C{^{1}H} NMR resonances of the carbonyl groups are very broad and are attributable to the large quadrupole moments of the rhenium isotopes. Photolysis of $Re_2(CO)_{10}$ and dmsm in toluene produced a yellow solid and an orange solution. The yellow solid was poorly soluble in CH_2Cl_2, and the IR spectrum of this solution in the carbonyl region (Table 1) is very similar to that of ax-[$Re_2(CO)_9$(dpsm)], whilst the orange solution had an IR spectrum showing similar absorptions and also bands attributable to $Re_2(CO)_{10}$ (2070, 2011 and 1966 cm^{-1}). The poor solubility of the yellow solid hindered NMR studies, but the ^{13}C{^{1}H} NMR spectrum showed (Table 1), in addition to ill-defined δ(CO) resonances, three resonances with δ equal to -6.0, -1.5 and -0.5, which we ascribe to η^1-dmsm, (c.f.

Table 2
Selected bond lengths (Å) and angles (°) for [$Mn_2(CO)_6(dpsm)_2$]

Sb(1)–Mn(1)	2.487(2)	Sb(3)–Mn(1)	2.489(2)
Sb(2)–Mn(2)	2.500(2)	Sb(4)–Mn(2)	2.496(2)
Sb(1)–C(9)	2.110(13)	Sb(3)–C(27)	2.122(12)
Sb(1)–C(3)	2.132(11)	Sb(3)–C(33)	2.131(12)
Sb(1)–C(1)	2.146(12)	Sb(3)–C(2)	2.158(11)
Sb(2)–C(21)	2.143(11)	Sb(4)–C(45)	2.121(12)
Sb(2)–C(15)	2.166(12)	Sb(4)–C(39)	2.137(11)
Sb(2)–C(1)	2.174(11)	Sb(4)–C(2)	2.138(12)
Mn(1)–C(51)	1.768(15)	Mn(2)–C(55)	1.776(14)
Mn(1)–C(52)	1.774(13)	Mn(2)–C(56)	1.819(16)
Mn(1)–C(53)	1.814(15)	Mn(2)–C(54)	1.826(14)
Mn(1)–Mn(2)	3.098(2)		
C(9)–Sb(1)–C(3)	98.5(5)	C(27)–Sb(3)–C(33)	102.4(5)
C(9)–Sb(1)–C(1)	101.3(5)	C(27)–Sb(3)–C(2)	99.0(4)
C(3)–Sb(1)–C(1)	104.0(5)	C(33)–Sb(3)–C(2)	99.3(5)
C(21)–Sb(2)–C(15)	98.3(4)	C(45)–Sb(4)–C(39)	97.4(4)
C(21)–Sb(2)–C(1)	103.1(5)	C(45)–Sb(4)–C(2)	103.2(5)
C(15)–Sb(2)–C(1)	99.2(5)	C(39)–Sb(4)–C(2)	100.0(5)
C(51)–Mn(1)–Mn(2)	81.8(3)	C(55)–Mn(2)–Mn(1)	179.4(4)
C(52)–Mn(1)–Mn(2)	176.6(4)	C(56)–Mn(2)–Mn(1)	85.1(3)
C(53)–Mn(1)–Mn(2)	82.5(4)	C(54)–Mn(2)–Mn(1)	82.8(3)
Sb(1)–Mn(1)–Mn(2)	88.64(6)	Sb(4)–Mn(2)–Mn(1)	88.69(6)
Sb(3)–Mn(1)–Mn(2)	94.83(7)	Sb(2)–Mn(2)–Mn(1)	92.06(6)
Sb(1)–C(1)–Sb(2)	103.0(5)	Sb(4)–C(2)–Sb(3)	106.7(5)
C–C–C (phenyl)	117(1)–124(1)	O–C–Mn	175(1)–179(1)
Sb(1)–Mn(1)–Mn(2)–Sb(2)	29.76(6)	C(51)–Mn(1)–Mn(2)–C(54)	31.5(6)
Sb(3)–Mn(1)–Mn(2)–Sb(4)	26.63(7)		

$[Mo(CO)_5(\eta^1\text{-dmsm})]$ [3]). The complex is unstable in solution, and the IR spectrum changes with time, possibly due to the air-sensitivity of the free -$SbMe_2$ group, and attempts to purify the bulk product by column chromatography were unsuccessful. An analytically pure sample was obtained by fractional crystallisation from CH_2Cl_2 under nitrogen.

4. Conclusions

This study completes our examination of distibinomethane metal carbonyl complexes [3,4]. Although similar complexes of diphosphinomethanes are known [9,10], the $[Mn_2(CO)_6(dpsm)_2]$ is an unusual example of direct substitution of more than one CO/metal by these distibines, and its facile photochemical synthesis contrasts with the preparation of $[Mn_2(CO)_8(dpsm)]$ by catalytic routes [4]. The reluctance of $Re_2(CO)_{10}$ to substitute more than one carbonyl group by a distibinomethane parallels the results obtained with Ph_3Sb, reflecting the much lower reactivity of the rhenium compound. Diphosphinomethanes, in contrast, produce $[Re_2(CO)_{10-2n}(\text{diphosphine})_n]$ ($n=1$ or 2) [9], reflecting their much higher basicity. In addition to providing further examples of two of the coordination modes identified earlier, this study has also confirmed the surprising resistance of these ligands to Sb–C fragmentation, even under photochemical conditions of synthesis of the complexes. Indeed, fragmentation seems much more facile in some platinum metal halide systems [13].

Supplementary data

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 117387. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk).

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References

[1] R.J. Puddephatt, Chem. Soc. Rev. 12 (1983) 99.
[2] N.R. Champness, W. Levason, Coord. Chem. Rev. 133 (1994) 115.
[3] A.M. Hill, N.J. Holmes, A.R.J. Genge, W. Levason, M. Webster, S. Rutschow, J. Chem. Soc., Dalton Trans. (1998) 825.
[4] A.M. Hill, W. Levason, M. Webster, I. Albers, Organometallics 16 (1997) 5641.
[5] N.J. Holmes, W. Levason, M. Webster, J. Organomet. Chem. 568 (1998) 213.
[6] R.H. Blessing, Acta Crystallogr., Sect. A 51 (1995) 33.
[7] G.M. Sheldrick, SHELXS86, Program for the Solution of Crystal Structures, University of Göttingen, 1985.
[8] G.M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, 1997.
[9] C.A. Morgan, P.E. Fanwick, I.P. Rothwell, Inorg. Chim. Acta 224 (1994) 105.
[10] R.B. King, K.S. RaghuVeer, Inorg. Chem. 23 (1984) 2482.
[11] M. Martin, B. Rees, A. Mitschler, Acta Crystallogr., Sect. B 38 (1982) 6.
[12] B.F. Hoskins, R.J. Steen, Aust. J. Chem. 36 (1983) 683.
[13] A.F. Chiffey, J. Evans, W. Levason, M. Webster, Organometallics 14 (1995) 1522, and unpublished work.