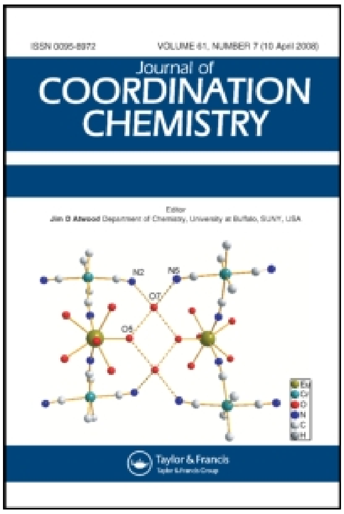


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and spectroscopic characterization of tris{(diphenylphosphino) dimethylsilyl}methane complexes of cr(0) and w(0)

Sushil K. Gupta[a]; Smita Pandey[a]
[a] School of Studies in Chemistry, Jiwaji University, Gwalior-474 011, India

To cite this Article Gupta, Sushil K. and Pandey, Smita(2004) 'Synthesis and spectroscopic characterization of tris{(diphenylphosphino) dimethylsilyl}methane complexes of cr(0) and w(0)', Journal of Coordination Chemistry, 57: 9, 785 — 790

To link to this Article: DOI: 10.1080/00958970410001721673
URL: http://dx.doi.org/10.1080/00958970410001721673

J. Coord. Chem., Vol. 57, No. 9, 15 June 2004, pp. 785–790

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF TRIS{(DIPHENYLPHOSPHINO) DIMETHYLSILYL}METHANE COMPLEXES OF Cr(0) AND W(0)

SUSHIL K. GUPTA* and SMITA PANDEY

School of Studies in Chemistry, Jiwaji University, Gwalior-474 011, India

(Received in final form 27 January 2004)

Treatment of $M(CO)_6$ ($M = Cr$, W) with $(Ph_2PMe_2Si)_3CH$ in toluene at elevated temperatures resulted in the isolation of pale green $[Cr(CO)_3\{(Ph_2PMe_2Si)_3CH\}]$ and pale brown $[W(CO)_3\{(Ph_2PMe_2Si)_3CH\}]$ in high yield. These complexes have been characterized by elemental analysis, conductivity measurements, TGA, mass spectrometry, and IR, electronic, ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The complexes have pseudo octahedral geometry around the metal atom with tridentate coordination of the multidentate ligand. The six-membered MPSiCSiP metallacycles are shown to have high fluxionality at room temperature on the NMR time scale.

Keywords: Tris{(diphenylphosphino)dimethylsilyl}methane; Tricarbonyl complexes; Chromium; Tungsten; Synthesis; NMR

INTRODUCTION

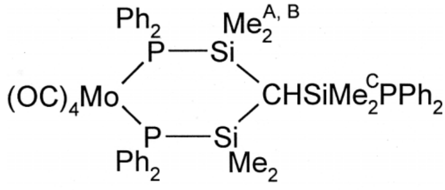
Tripodal phosphines are excellent ligating agents for transition metals and complexes have been synthesized for the study of structure-bonding relationships and applications in catalysis [1–3]. The nature of the backbone in polydenate phosphines is of importance in determining the stereochemistry imposed by the ligand on the metal [4,5]. Extensive studies have been focused on the synthesis of Group 6 metal carbonyl complexes with tripodal phosphine ligands based on cyclohexane. These include $[Mo(tdppcy)(CO)_3]$, [Ir(tdppcy)(CO)Cl] (tdppcy = *cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane) [6], $[Mo(tdppcycn)(CO)_3]$, [Ir(tdppcycn)(CO)Cl] (tdppcycn = *cis,cis*-1,3,5-tris(cyano)-1,3,5-tris(diphenylphosphanyl)cyclohexane) [7] and $[Mo(tdppcyme)(CO)_3]$ (tdppcyme = *cis,cis*-1,3,5-tris(diphenylphophino)-1,3,5-tris(methoxycarbonyl)cyclohexane [8,9], in which the ligand is assigned as being tridentate. King *et al.* have reported [10,11] the synthesis of $[M(CO)_4L]$ and $[M(CO_3)L]$

---

*Corresponding author. Fax: +91 751 2341450. E-mail: drskgcy@sancharnet.in

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001721673

(M = Cr, Mo; L = bis(2-diphenylphosphinoethyl)phenylphosphine), in which the ligand L is bidentate and tridentate, respectively. The compounds $[Co(OAc)L][BPh_4]$ and $[Fe(CH_3CN)_2L][BF_4]_2$, showing tridentate ligation of $HC(CH_2PPh_2)_3$, L, have been structurally characterized [12], showing tridentate ligation of L. We have previously reported [13] the synthesis of tris{(diphenylphosphino)dimethylsilyl}methane, $[HC(PPh_2Me_2Si)_3]$ and its tetracarbonyl molybdenum Complex **1**, in which coordination of the ligand is bidentate.



Complex **1**

In the present study we describe the ligating behaviour of the tripodal ligand $HC(SiMe_2PPh_2)_3$ with other Group 6 metal carbonyls.

EXPERIMENTAL

All reactions were conducted under an argon atmosphere by the use of standard Schlenk techniques on a double manifold vacuum line. Solvents were purified by distillation from an appropriate drying agent (toluene and THF from potassium, hexane from Na/K alloy). Chromium and tungsten hexacarbonyls were obtained from Aldrich. The ligand was synthesized as published earlier [13].

Physical Measurements

Melting points were recorded in capillary tubes and are uncorrected. Elemental analyses were performed with a Carlo-Erba model DP 200 instrument. Thermogravimetric analysis was carried out on a DuPont TGA 2950 analyser in synthetic air atmosphere with a heating rate of $10°C\,min^{-1}$. Molar conductance in $10^{-3}\,mol\,dm^{-3}$ DMF solution was measured using a Global DCM-900 digital conductivity meter. IR spectra were recorded on a Perkin-Elmer 1720 FT IR spectrometer with KBr pellets and in CH_2Cl_2 solution. EI mass spectra were recorded with a VG Autospec spectrometer at 70 eV: m/z values are given for ^{1}H, ^{12}C, ^{28}Si, ^{52}Cr and ^{184}W. Electronic spectra in $10^{-4}\,mol\,dm^{-3}$ DMF solutions were obtained using a Shimadzu UV-160A recording spectrophotometer. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were recorded in DMSO-d_6 at 300 and 121.4 MHz, respectively, on a Bruker 300 MHz NMR instrument and chemical shifts are relative to $SiMe_4$ for H and H_3PO_4 for P.

Tricarbonyl[tris{(diphenylphosphino)dimethylsilyl}methane]chromium(0) $[Cr(CO)_3\{(Ph_2PMe_2Si)_3CH\}]$ (2)

A solution of $[Cr(CO)_6]$ (0.266 g, 1.21 mmol) and $(Ph_2PMe_2Si)_3CH$ (0.898 g, 1.21 mmol) in toluene ($75\,cm^3$) was slowly heated under reflux, then maintained at reflux for 48 h to give a pale green solution. The solution was allowed to cool to room temperature and solvent removed to leave a pale green solid. Yield: 0.21 g (87%); m.p. 246°C (dec.). *Anal.* Found (%): C, 61.80; H, 5.76. Calc. for $C_{46}H_{49}P_3Si_3O_3Cr$: C, 62.79; H, 5.57. MS (EI) (*m*/*z*): 878 [1%, M]$^+$, 850 [3%, M – CO]$^+$, 822 [1%, M – 2CO]$^+$, 794 [5%, M – 3CO]$^+$, 703 [10%, M – H – 3SiMe$_2$]$^+$, 629 [25%], 555 [28%], 370 [36%], 201 [100%]-(ligand fragments). IR (cm^{-1}): 1928, 1895 (in KBr)/1932, 1899 (in CH_2Cl_2) [ν(CO)]. ^{1}H NMR ($CDCl_3$): δ 0.08 (s, 18H, SiMe$_2$), 2.09 (s, 1H, CH), 7.05–7.59 (m, 30H, Ph). ^{31}P{^{1}H} NMR: δ 36.7.

Tricarbonyl[tris{(diphenylphosphino)dimethylsilyl}methane]tungsten (0) [W(CO)$_3${(Ph$_2$PMe$_2$Si)$_3$CH}] (3)

A solution of [W(CO)$_6$] (0.522 g, 1.48 mmol) and (Ph$_2$PMe$_2$Si)$_3$CH (1.10 g, 1.48 mmol) in toluene (75 cm^3) was slowly heated under reflux, then maintained at reflux for 68 h to give a brown solution. The solution was allowed to cool to room temperature and solvent removed to leave a brown, sticky solid. It was treated with petroleum ether (40–60°C) to obtain a pale brown solid. Yield: 0.75 g (81%); m.p. 152°C (dec.). *Anal.* Found (%): C, 55.14; H, 5.01. Calc. for $C_{46}H_{49}P_3Si_3O_3W$: C, 54.60; H, 4.85. MS (EI) (*m*/*z*): 995 [12%, M – Me]$^+$, 926 [5%, M – H – 3CO]$^+$, 849 [35%, M – 3HCO – SiMe$_3$H]$^+$, 775 [100%, M – 3HCO – 2SiMe$_3$H]$^+$. IR (cm^{-1}): 1935, 1903 (in KBr/CH_2Cl_2) [ν(CO)]. ^{1}H NMR ($CDCl_3$): δ 0.14 (s, 18H, SiMe$_2$), 1.19 (s, 1H, CH), 7.29–7.69 (m, 30H, Ph). ^{31}P{^{1}H} NMR: δ 34.1.

RESULTS AND DISCUSSION

Synthesis and Properties

The reactivity of tris{(diphenylphosphino)dimethylsilyl}methane, [CH(SiMe$_2$PPh$_2$)$_3$], a sterically hindered tripodal ligand towards Group 6 metal carbonyls, has been examined. Pale green chromium and pale brown tungsten complexes that appear from analytical data and from the spectroscopic results described below to have the composition [M(CO)$_3${(Ph$_2$PMe$_2$Si)$_3$CH}] (M = Cr (**2**); W(**3**)) have been obtained in almost quantitative yield. Complexes **2** and **3** behave as non-electrolytes in DMF.

Mass Spectra

The EI mass spectrum of Complex **2** exhibits a weak molecular ion peak at *m*/*z* 878 formed by initial ionization, which fits the molecular formula [$C_{46}H_{49}P_3Si_3O_3Cr$]. Peaks at *m*/*z* 850, 822, 794, 703 and 629 are due to the successive loss of three CO groups, as expected for a complex containing the [Cr(CO)$_3$] moiety [14]. Other important peaks at *m*/*z* 555, 370 and 201 have the similar fragmentation pattern as observed in the ligand.

The EI mass spectrum of **3** did not exhibit the expected molecular ion peak at *m*/*z* 1010; instead it showed peaks at 995 and 926 arising due to rapid loss of one CH_3 and 3CO, respectively, from the molecular ion peak (M$^+$). The loss of three CO units from the parent molecular ion peak indicates the presence of [W(CO)$_3$] in the complex. Other important peaks at *m*/*z* 849 and 775 are due to the loss of (3HCO + SiMe$_3$H) and

$(3HCO + 2SiMe_3H)$, respectively. The isotopic pattern of each of the peaks confirms the presence of tungsten.

Thermal Study

The chromium and tungsten complexes were studied by thermogravimetric analysis (TGA) under a dynamic air atmosphere in the temperature region 30 to 680°C at a heating rate of $10°C\,min^{-1}$. Complex **2** starts to evolve CO at 230°C and registers a mass loss of 9.1% at 350°C compared with the theoretical value of 9.5%, which corresponds to the loss of three coordinated CO molecules. From 350 to 425°C, a mass loss of 16.7%, compared with the theoretical value of 15.8%, is attributed to the combined loss of three CO + Cr. The total mass loss (53.7%) at 507°C is for ligand degradation. The high residual mass (46.3%; *ca* 42.8%) indicates the formation of carbonaceous matter with metal oxide, Cr_2O_3, and tris(dimethylsiloxane), $(Me_2SiO)_3$. Complex **3** registers a mass loss of 5.3% (theoretical 5.5%) at 158.6°C and 8.3% (theoretical 8.3%) at 220.6°C, attributed to the loss of 2CO and 3CO respectively. At 272.3°C, a mass loss of 17.0% compared with the theoretical value of 17.2% is observed for the loss of $3SiMe_2$. The combined mass loss of 26.5% (theory 26.5%) corresponds to 3CO + W at 295.6°C. After 400°C the complex starts to decompose and total mass loss (85.7%) shows the formation of $(Me_2SiO)_2$. Thus the decomposition patterns confirm the proposed formulation of the complexes. The thermal stability sequence is in the order Cr(0) > W(0).

IR Spectra

IR spectra of Complexes **2** and **3** recorded in solution (dichloromethane) and in the solid state (KBr) exhibited two terminal C–O stretching vibrations consistent with the A_1 and E modes expected for a pseudo C_{3v}, X_3MY_3 coordination structure [15–19]. The pattern is characteristic of a complex in which the $[M(CO)_3]$ moiety is attached to a triphosphine ligand [2,11,20]. The ν(CO) bands are similar to those reported for the related compounds, $[\{(Ph_2PCH_2CH_2)_2PPh\}M(CO)_3]$ (M = Cr [21], W[10]) $[CH(CH_2PPh_2)_2]_2Cr(CO)_3$ [22], $[W(CO)_3\{$*cyclo*-$(Me_3SiCH_2PC_3H_6)_3\}]$ [23], $[\{CH(Ph_2P)_2CH_2PPh_2\}W(CO)_3]$ [24,25], $[W(CO)_3L^3]$ ($L^3 = MeC(CH_2SMe)_3$) [26].

Electronic Spectra

The UV spectrum of the multidentate ligand in 10^{-3} M DMF solution shows a prominent band with λ_{max} 271 nm. Electronic spectra of **2** and **3** in 10^{-3} M DMF solutions exhibit only one d–d band at 614 ($\varepsilon = 261\,M^{-1}\,cm^{-1}$) and 506 ($\varepsilon = 36\,M^{-1}\,cm^{-1}$) nm, respectively. This band seems to have major contribution from the $t_{2g} \rightarrow e_g$ ($^1A_{1g} \rightarrow {}^1E_g$) transition for a d^6 low spin complex [27]. In addition, both the complexes show very intense absorptions in the UV region, possibly due to intraligand transitions as observed in the free ligand at similar energies. These observations are consistent with the octahedral structure of the complexes.

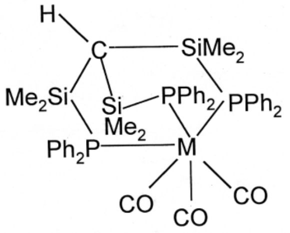


FIGURE 1 Proposed structure of the Complexes **2** and **3**.

^{1}H NMR Spectra

^{1}H NMR spectra of the Complexes **2** and **3** in dmso-d_6 showed peaks for the methylene and methine protons. The presence of singlet peaks and absence of phosphorous–hydrogen coupling clearly indicate that all the $\mathrm{SiMe_2PPh_2}$ groups lie in the same chemical environment.

^{31}P{^{1}H} NMR

^{31}P{^{1}H} NMR spectra of the Complexes **2** and **3** at room temperature display a sharp singlet at δ 36.7 and 34.1, respectively. The single chemical shift values in **2** and **3** are indicative of the equivalence of the three phosphorus atoms [28]. Observed chemical shifts are typical for coordinated phosphines of this type [12]. The coordination chemical shifts are 87.7 ppm for **2** and 84.1 ppm for **3**. Thus the ^{31}P NMR spectra confirm the tridentate ligation of the triphosphine ligand.

Proposed Structure of the Complexes

The above mentioned evidence indicates an octahedral geometry around the metal with tridentate coordination of phosphine ligand. Proposed structures are shown in Fig. 1. Similar structures have been reported for $[\mathrm{M(CO)_3\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_2)_2\}}]$ (M = Cr or W) [29], $[\mathrm{Cr(CO)_3\{HCCH_2(PPh_2)_3\}}]$ [24,25], $[\mathrm{W(CO)_3}\{cyclo\text{-}\mathrm{(Me_3SiCH_2PC_3H_6)_3}\}]$ [23] and $[\mathrm{\{(Ph_2PCH_2CH_2)_2PPh\}W(CO)_3}]$ [10]. Attempts to grow good quality single crystals of any of these compounds were unsuccessful.

It is interesting to observe that the tripodal phosphine ligand acts as bidentate with molybdenum and as a tridentate with chromium and tungsten. The bidentate and tridentate coordination of the ligand in **1**, **2** and **3** give a six-membered MPSiCSiP metallacycle.

Acknowledgments

We are grateful to the Department of Science and Technology (DST), New Delhi, for financial assistance and Prof. Colin Eaborn and Dr. J. D. Smith for their encouragement and constant inspiration. We acknowledge the help of Dr. A. Abdul-Sada and Dr. A. G. Avent in recording mass and NMR spectra, respectively.

References

[1] W. Levason, In S. Patai and F.R. Hartley (Eds.), The Chemistry of Organophosphorus Compounds (Wiley, New York, 1990), p. 556.
[2] H.A. Mayer and W.C. Kaska, *Chem. Rev.* **94**, 1239 (1994).
[3] C. Bianchini and A. Meli, *Acc. Chem. Res.* **31**, 109 (1999).
[4] M. Antberg and L. Dahlenburg, *Inorg. Chim. Acta* **104**, 51 (1985).
[5] C. Bianchini, F. Laschi, D. Masi, F.M. Ottaviani, A. Pastor, M. Peruzzini, P. Zanello and F. Zanobini, *J. Am. Chem. Soc.* **115**, 2723 (1993).
[6] H.A. Mayer, H. Otto, H. Kuhbauch, R. Fawzi and M. Steimann, *J. Organomet. Chem.* **472**, 347 (1994).
[7] H.A. Mayer, P. Stobel, R. Fawzi and M. Steimann, *Chem. Ber.* **128**, 719 (1995).
[8] P. Stossel, H.A. Mayer, C.M. Mossmev, R. Fawzi and M. Steimann, *Inorg. Chem.* **35**, 5860 (1996).
[9] H.A. Mayer, P. Stobel, R. Fawzi and M. Steimann, *J. Organomet. Chem.* **492**, C1 (1995).
[10] R.B. King, *Acc. Chem. Res.* **5**, 177 (1972).
[11] R.B. King, P.N. Kapoor and R.N. Kapoor, *Inorg. Chem.* **10**, 1841 (1971).
[12] B.C. Janseen, A. Asam, G. Huttner, V. Sernau and L. Zsolnai, *Chem. Ber.* **127**, 501 (1994).
[13] A.G. Avent, D. Bonafaux, C. Eaborn, S.K. Gupta, P.B. Hitchcock and J.D. Smith, *J. Chem. Soc., Dalton Trans.* 831 (1999).
[14] J.E. Ellias, *J. Organomet. Chem.* **86**, 1 (1975).
[15] F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry (Wiley, New York, 1988), 5th Edn., p. 64.
[16] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds (Wiley, New York, 1997), 5th Edn., p. 135.
[17] E.W. Abel, M.A. Bennett and G. Wilkinson, *J. Chem. Soc.* 2323 (1959).
[18] A.A. Chalmers, J. Lewis and R. Whyman, *J. Chem. Soc.* 1817 (1967).
[19] J.G. Bullit, F.A. Cotton and T.J. Marks, *Inorg. Chem.* **11**, 671 (1972).
[20] J.T. Mague and S.E. Dessens, *J. Organomet. Chem.* **262**, 347 (1984).
[21] M.R. Mason, C.M. Duff, R.A. Jacobson and J.G. Verkade, *Inorg. Chem.* **31**, 2746 (1992).
[22] L. Dahlenburg and F. Mirzaei, *Inorg. Chim. Acta* **97**, L1 (1985).
[23] S.J. Coles, P.G. Edwards, J.S. Fleming and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.* 1139 (1995).
[24] J.L. Bookham, W. McFarlane, I.J. Colquhoun and M. Thornton-Pett, *J. Organomet. Chem.* **354**, 313 (1988).
[25] J.L. Bookham, W. McFarlane and I.J. Colquhoun, *J. Chem. Soc., Dalton Trans.* 503 (1988).
[26] A.J. Barton, J. Connolly, W. Levason, A. Mendia-Jalon, S.D. Orchard and G. Reid, *Polyhedron* **19**, 1373 (2000).
[27] E.I. Solomon and A.B.P. Lever, Inorganic Electronic Structure and Spectroscopy (Wiley, New York, 1999), Vol. II, p. 543.
[28] J.G. Verkade and L.D. Quin, Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis (VCH, Florida, 1987).
[29] V. Caliman, P.B. Hitchcock, J.F. Nixon, L. Nyulaszi and N. Sakarya, *J. Chem. Soc., Chem. Commun.* 1305 (1997).