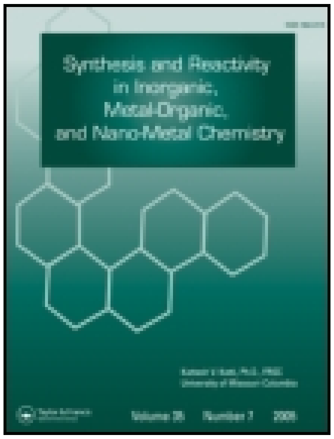
This article was downloaded by: [New York University]
On: 13 December 2014, At: 21:13
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Spectroscopic and Electrochemical Studies of Group 6 and 8 Transition Metal Carbonyl Derivatives of tris{(diphenylphosphinomethyl)dimethylsilyl}methane

Sushil K. Gupta [a] & Siddhi Nigam [a]
[a] School of Studies in Chemistry, Jiwaji University , Gwalior , India

Accepted author version posted online: 17 Apr 2013.Published online: 14 May 2013.

To cite this article: Sushil K. Gupta & Siddhi Nigam (2013) Spectroscopic and Electrochemical Studies of Group 6 and 8 Transition Metal Carbonyl Derivatives of tris{(diphenylphosphinomethyl)dimethylsilyl}methane, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 43:9, 1175-1180, DOI: 10.1080/15533174.2012.756900

To link to this article: http://dx.doi.org/10.1080/15533174.2012.756900

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 43:1175–1180, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2012.756900

Spectroscopic and Electrochemical Studies of Group 6 and 8 Transition Metal Carbonyl Derivatives of tris{(diphenylphosphinomethyl)dimethylsilyl}methane

Sushil K. Gupta and Siddhi Nigam
School of Studies in Chemistry, Jiwaji University, Gwalior, India

A new series of transition metal carbonyl complexes of tris{(diphenylphosphinomethyl)dimethylsilyl}methane are described in this work. Treatment of $M(CO)_6$ (M = Cr, W, Mo) and $Fe_2(CO)_9$ with $[(Ph_2PCH_2Me_2Si)_3CH]$ in tetrahydrofuran at elevated temperature resulted in the isolation of $[M(CO)_3\{(Ph_2PCH_2Me_2Si)_3CH\}]$ (M = Cr(1), Mo(2), W(3), Fe(4)) in good yield. These complexes have been characterized by elemental analysis, conductivity measurements, mass spectrometry, with IR, electronic, ^1H and ^{31}P NMR spectroscopy, and cyclic voltammetry. The data suggest that complexes 1, 2, 3, and 4 have octahedral geometry around the metal atom with tridentate coordination of the ligand. Electrochemical studies of 1, 2, 3, and 4 using cyclic voltammetry indicate quasireversible metal centered oxidation ($E^{\circ\prime}$ −1.217 V(1), −1.218 V(2), −1.166 V(3), and −1.258 V(4) versus Ag/Ag^+) and ligand reductions (0.292 V, 0.170 V, −0.331 V, and 0.338 V versus Ag/Ag^+).

Keywords cyclic voltammetry, M(0)-carbonyl (M = Cr, Mo, W, Fe), NMR, tris{(diphenylphosphinomethyl}-dimethylsilyl) methane

INTRODUCTION

Polydentate phosphine ligands have received attention because of their rich coordination chemistry and the catalytic application of their metal complexes.[1–3] We have been exploring the chemistry of sterically hindered tripodal phosphine ligands of the type $(Ph_2PMe_2Si)_3CH$ and $(Ph_2PCH_2Me_2Si)_3CH$ with main group and transition metals. The lithium compound, $[Li(tmen)_2][C(SiMe_2PPh_2)_3]$, obtained by metallation of the precursor $(Ph_2PMe_2Si)_3CH$ has discrete planar carbanions and no Li—P coordination.[4,5] However, the lithium compound with a $[LiC(SiMe_2CH_2PPh_2)_3]$ precursor has an unusual tricyclic structure with lithium bound to a carbanionic center and three phosphorus atoms.[6] Carbonyl complexes have received less attention[7,8] and reports are currently limited to our studies of $[M(CO)_3\{(Ph_2PMe_2Si)_3CH\}]$[9] where M = Cr and W and *cis*-$[Mo(CO)_4\{(Ph_2PMe_2Si)_3CH\}]$[4] and $[MCl_2\{(Ph_2PMe_2Si)_3CH\}]$[10] (M = Mn(II) and Fe(II)). The tripodal ligand is bidentate toward molybdenum and tridentate toward chromium, tungsten, manganese, and iron. In the present study, we describe the ligating behavior of the tripodal ligand, $(Ph_2PCH_2Me_2Si)_3CH$ with $M(CO)_6$ (M = Cr, W, Mo) and $Fe_2(CO)_9$. We also report our findings on the electrochemical behavior of these carbonyl complexes.

EXPERIMENTAL

All reactions were conducted under an argon atmosphere by the use of standard Schlenk techniques on a double manifold vacuum line.[11,12] All the chemicals were of reagent grade and were used as received. Chromium, molybdenum and tungsten hexacarbonyls and $Fe_2(CO)_9$ were obtained from Aldrich (India). The ligand, $(Ph_2PCH_2Me_2Si)_3CH$, was synthesized following the reported method.[6] Solvents were purified by standard methods.[13]

Physical Measurements

Melting points were recorded in capillary tubes and are uncorrected. Elemental analyses were obtained with a Carlo-Erba model DP 200 instrument (United Kingdom). Molar conductances in 10^{-4} mol dm^{-3} MeCN solution were measured using a Global DCM-900 digital conductivity meter (Global Electronics, India). The IR spectra were obtained in KBr pellets on a Shimadzu Prestise-21 FT IR spectrometer (Japan). The FAB mass spectra were recorded in the positive mode on a JEOL SX-102 mass spectrometer (Japan) using 3-nitrophenyl methanol (*m*-nitrobenzyl alcohol, *m*-NBA) as the matrix: *m/z* values are given for ^1H, ^{12}C, ^{16}O, ^{28}Si, ^{31}P, ^{52}Cr, ^{98}Mo, and ^{184}W. The samples dissolved in ($CHCl_3$/MeOH/EtOH) were introduced into the FAB source.

Received 2 September 2012; accepted 4 December 2012.

The authors are grateful to the University Grants Commission (UGC), New Delhi for financial assistance (grant number: F.12–132/2001 (SR-I)) and for the award of a fellowship to S.N. They thank SAIF, CDRI, Lucknow, for recording mass spectra and BHU, Varanasi, for NMR spectra as well as Dr. J. D. Smith, University of Sussex, England, for discussion. The authors also thank the reviewers for their constructive suggestions.

Address correspondence to Sushil K. Gupta, School of Studies in Chemistry, Jiwaji University, Gwalior 474011, India. E-mail: skggwr@gmail.com

The electronic spectra in 10^{-4} mol dm^{-3} C_6H_6 solution were obtained by use of a Shimadzu UV-160A recording spectrophotometer (Japan). The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a 300 MHz JEOL AL 300 FT NMR instrument (Japan) at 300.4 (^1H) and 121.5 MHz (^{31}P) and chemical shifts are relative to $SiMe_4$ for H and H_3PO_4 (85%) for P.

Electrochemical Measurements

Cyclic voltammetric measurements were carried out with an Advanced Electrochemical System, the PARSTAT 2253 instrument (Princeton Applied Research, USA) equipped with a three-electrode system. The microcell model KO264 consisted of a glassy carbon working electrode with Pt wire as an auxiliary electrode and a nonaqueous $Ag/AgNO_3$ reference electrode with 0.1 M $AgNO_3$ in acetonitrile as a filling solution. Tetrabutylammonium perchlorate (TBAP) (0.1 M solution in CH_3CN) was used as the supporting electrolyte. Cyclic voltammograms with scan speeds of 100–500 mV s^{-1} were run in 10^{-4} M CH_3CN solution under a nitrogen atmosphere. The potentials measured against an Ag/Ag^+ reference electrode were compared to those for the ferrocene-ferrocenium couple, which under the same experimental conditions gave $E_{1/2} = 0.5(E_{pa} + E_{pc}) = 0.048$V and $\Delta E_p = (E_{pa} - E_{pc}) = 80$ mV.

Synthesis of Tricarbonyl[tris{(diphenylphosphinomethyl) dimethylsilyl}methane] chromium(0) [$Cr(CO)_3\{(Ph_2PCH_2Me_2Si)_3CH\}$] (1)

To a solution of $Cr(CO)_6$ (0.149 g, 0.677 mmol) in THF (50 mL) was added dropwise a solution of $(Ph_2PCH_2Me_2Si)_3CH$ (0.531 g, 0.677 mmol) in THF (50 mL) at room temperature and the mixture was slowly heated to reflux for 72 h. After cooling, a greenish yellow precipitate of [$Cr(CO)_3\{(Ph_2PCH_2Me_2Si)_3CH\}$] was filtered off, washed with light petroleum (40–60°C), and dried *in vacuo*. Yield: 0.396 g (64%), m.p. 206°C (dec.). Anal. Calcd. for $C_{49}H_{55}P_3Si_3O_3Cr$ (%): C, 63.9; H, 5.9; P, 10.1. Found: C, 63.6; H, 6.2; P, 10.7. MS (FAB$^+$) (*m/z*): 920 [M$^+$]. Λ_M (10^{-4} M, CH_3CN, 298 K): 50 S cm^{2}mol^{-1}. IR (KBr, ν (cm^{-1})):1925, 1815 [ν(CO)], 1261 [δ(C – H)], 1022, 866, 748 [ρ(H_3C)Si], 663 [ν_{as}(Si –C)], 610 [ν_s(Si –C)]. UV-Vis (CH_3CN, λ (nm)): 270, 305. ^1H NMR ($CDCl_3$, δ (ppm)): –0.11 (s, CH), 0.07 (s, $SiMe_2$), 1.25 (s, CH_2), 7.25–7.73 (m, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ (ppm)): 0.6 (s, PPh_2). CV data: $E^{\circ\prime}(1)$ –1.217 V; $E^{\circ\prime}(2)$ 0.292 V.

Synthesis of Tricarbonyl[tris{(diphenylphosphinomethyl) dimethylsilyl}methane] molybdenum(0) [$Mo(CO)_3\{(Ph_2PCH_2Me_2Si)_3CH\}$] (2)

A solution of $Mo(CO)_6$ (0.155 g, 0.587 mmol) in THF (45 mL) was added dropwise to a solution of $(Ph_2PCH_2Me_2Si)_3CH$ (0.460 g, 0.587 mmol) in THF (45 mL) at room temperature and the mixture was slowly heated to reflux for 48 h. After cooling, a pale yellow precipitate of [$Mo(CO)_3\{(Ph_2PCH_2Me_2Si)_3CH\}$] was filtered off, washed with light petroleum (40–60°C), and dried *in vacuo*. Yield: 0.267 g (59%), m.p. 224°C (dec.). Anal. Calc. for $C_{49}H_{55}P_3Si_3O_3Mo$ (%): C, 60.8; H, 5.7; P, 9.6. Found: C, 61.2; H, 5.8; P, 10.0. MS (FAB$^+$) (*m/z*): 966 [M$^+$]. Λ_M (10^{-4} M, CH_3CN, 298 K): 30 S cm^{2}mol^{-1}. IR (KBr, ν (cm^{-1})):1938, 1815 [ν(CO)], 1261 [δ(C – H)], 1022, 864, 756 [ρ(H_3C)Si], 694 [ν_{as}(Si –C)], 610 [ν_s(Si –C)]. UV-Vis (CH_3CN, λ (nm)): 273, 324. ^1H NMR ($CDCl_3$, δ (ppm)): –0.10 (s, CH), 0.06 (s, $SiMe_2$), 1.25 (s, CH_2), 7.25–7.77 (m, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ (ppm)): 3.8 (s, PPh_2). CV data: $E^{\circ\prime}(1)$ –1.218 V; $E^{\circ\prime}(2)$ 0.170 V.

Synthesis of Tricarbonyl[tris{(diphenylphosphinomethyl) dimethylsilyl}methane] tungsten(0) [$W(CO)_3\{(Ph_2PCH_2Me_2Si)_3CH\}$] (3)

A solution of [$W(CO)_6$] (0.278 g, 0.789 mmol) and $(Ph_2PCH_2Me_2Si)_3CH$ (0.619 g, 0.789 mmol) in THF (100 mL) was slowly heated to reflux for 22 h. After cooling, a dark yellow precipitate of [$W(CO)_3\{(Ph_2PCH_2Me_2Si)_3CH\}$] was filtered off, washed with light petroleum (40 – 60°C) and dried *in vacuo*. Yield: 0.415 g (90%), m.p. 248°C (dec.). Anal. Calcd. for $C_{49}H_{55}P_3Si_3O_3W$ (%): C, 55.8; H, 5.2; P, 8.8. Found: C, 56.2; H, 5.4; P, 9.3. MS (FAB$^+$) (*m/z*): 1052 [M$^+$]. Λ_M (10^{-4} M, CH_3CN, 298 K): 10 S cm^{2}mol^{-1}. IR (KBr, ν (cm^{-1})):1919, 1815 [ν (CO)], 1261 [δ (C – H)], 1024, 868, 748 [ρ (H_3C)Si], 694 [ν_{as} (Si –C)], 610 [ν_s (Si –C)]. UV-Vis (CH_3CN, λ (nm)): 273, 311. ^1H NMR ($CDCl_3$, δ (ppm)): –0.10 (s, CH), 0.00 (s, $SiMe_2$), 1.22 (s, CH_2), 7.19–7.66 (m, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ (ppm)): 4.1 (s, PPh_2). CV data: $E^{\circ\prime}(1)$ –1.166 V; $E^{\circ\prime}(2)$ –0.331 V.

Synthesis of Tricarbonyl[tris{(diphenylphosphinomethyl) dimethylsilyl}methane] iron(0) [$Fe(CO)_3\{(Ph_2PCH_2Me_2Si)_3CH\}$] (4)

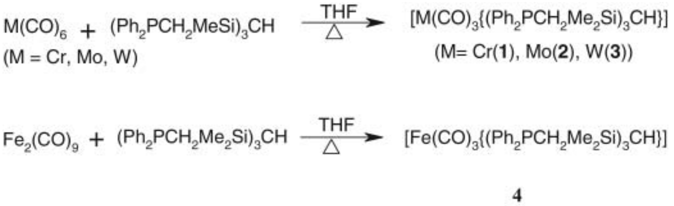
A solution of [$Fe_2(CO)_9$] (0.225 g, 0.618 mmol) and, $(Ph_2PCH_2Me_2Si)_3CH$ (0.485 g, 0.618 mmol) in THF (100 cm^3) was slowly heated to reflux for 43 h. After cooling a reddish brown solid of [$Fe(CO)_3\{(Ph_2PCH_2Me_2Si)_3CH\}$] was filtered off, washed with light petroleum (40–60°C), and dried *in vacuo*. Yield: 0.289 g (72%), m.p. 304°C (dec.). Anal. Calcd. for $C_{49}H_{55}P_3Si_3O_3Fe$ (%): C, 63.6; H, 5.9; P, 10.1. Found: C, 64.1; H, 6.2; P, 10.8. MS (FAB$^+$) (*m/z*): 924 [M$^+$]. Λ_M (10^{-4} M, CH_3CN, 298 K): 60 S cm^{2}mol^{-1}. IR (KBr, ν (cm^{-1})):1937, 1815 [ν (CO)], 1261 [δ (C – H)], 1022, 869, 748 [ρ (H_3C)Si], 694 [ν_{as} (Si –C)], 610 [ν_s (Si –C)]. UV-Vis (CH_3CN, λ (nm)): 273, 330. ^1H NMR ($CDCl_3$, δ (ppm)): –0.10 (s, CH), 0.00 (s, $SiMe_2$), 1.18 (s, CH_2), 7.19–7.66 (m, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ (ppm)): 12.6 (s, PPh_2). CV data: $E^{\circ\prime}(1)$ –1.258 V; $E^{\circ\prime}(2)$ 0.338 V.

RESULTS AND DISCUSSION

Synthesis and Properties

The reactivity of tris{(diphenylphosphinomethyl)dimethyl silyl}methane, [$(Ph_2PCH_2Me_2Si)_3CH$], a sterically hindered tripodal ligand, toward transition metal carbonyl complexes has been examined. Greenish yellow chromium, pale yellow molybdenum, dark yellow tungsten, and reddish brown iron

(Scheme 1) that appear from analytical data and from the spectroscopic results described subsequently with a composition of $[M(CO)_3\{(Ph_2PCH_2Me_2Si)_3CH\}]$ [M = Cr(**1**); Mo(**2**); W(**3**); Fe(**4**)] have been obtained in good yield. All the complexes are stable at room temperature, soluble in benzene, chloroform, DMSO and DMF and melt with decomposition in the temperature range 206–304°C. The molar conductance in acetonitrile is low compared to values reported[14] for 1:1 electrolytes (Λ_M 120–160 $S\ cm^2mol^{-1}$) suggesting that these are nonelectrolytes. Elemental analyses agreed well with the previous formulations.



SCH. 1.

Mass Spectra

The FAB mass spectrum of complex **1** exhibits a weak molecular ion peak with correct isotope pattern at *m/z* 920 which fits the molecular formula $[C_{49}H_{55}P_3Si_3O_3Cr]$. Peaks at *m/z* 892, 864, and 836 are due to successive loss of three carbonyl groups, as expected for a complex containing the $[Cr(CO)_3]$ moiety.[15] Other important peaks at *m/z* 712, 654, 572, 555, 498, 281, and 223 have a similar fragmentation pattern as observed in the ligand.

Complexes **2**, **3**, and **4** show molecular ion peaks at *m/z* 966, 1052, and 924, respectively, in their mass spectra. They also show successive loss of three CO groups at *m/z* 938, 910, 882 (**2**), 1024, 996, 968 (**3**), and 896, 868 and 840 (**4**), respectively. The isotopic pattern of each peak in **2, 3**, and **4** confirms the presence of molybdenum, tungsten, and iron.

IR Spectra

The IR spectra of complexes **1**, **2**, **3**, and **4** in the finger-print region (1200–700 cm^{-1}) are similar to that for the free ligand which confirms the presence of the ligand $HC(SiMe_2CH_2PPh_2)_3$ in these complexes. A medium intensity band at 1261 cm^{-1} is observed in all the complexes which is assigned to bending methyl vibrations, $\delta(CH_3)$. The bands at 1022–1024, 864–869, and 748–756 cm^{-1} are assigned to methyl-silicon rocking modes, $\rho(CH_3)(Si)$. The silicon-carbon (tertiary) asymmetric and symmetric stretching vibrations $\nu_{as}(SiC)$ and $\nu_s(SiC)$ are observed at 663–694 and 610 cm^{-1}, respectively. These assignments are in good agreement with related bulky silyl-substituted compounds.[16–18] All the complexes show two terminal C – O stretching vibrations consistent with A_1 and E modes expected for a pseudo C_{3v}, X_3MY_3 coordination structure.[19–23] The pattern is characteristic of a complex in which the $[M(CO)_3]$ moiety is attached to a triphosphine ligand.[3,7,24] The ν(CO) bands are similar to those reported for related compounds, $[M(CO)_3\{(Ph_2PMe_2Si)_3CH\}]$ (M = Cr, W),[9] $[\{(Ph_2PCH_2CH_2)_2PPh\}M(CO)_3]$ (M = Cr,[25] W[24]), $[CH(CH_2PPh_2)_2]_2Cr(CO)_3$,[26] $[W(CO)_3\{$*cyclo*-$(Me_3SiCH_2PC_3H_6)_3\}]$,[27] $[\{CH(Ph_2P)_2CH_2PPh_2\}W(CO)_3]$,[8,28] $[W(CO)_3L^3]$ ($L^3 = MeC(CH_2SMe)_3$),[29] and $[Fe(CO)_3(TPM)]$ (TPM = tris(diphenylphosphino)methane.[7]

Electronic Spectra

The electronic spectra of complexes **1**, **2**, **3**, and **4** show two characteristic bands, one at lower wavelength *ca.* 270 nm for an intraligand charge transfer (ILCT) transition and an intense broad band appearing at >300 nm. This longer wavelength transition is assigned to a MLCT band ($d(M(0) \rightarrow \pi^*$ (ligand)). The energy of the MLCT transition state of the compounds follows the order Cr > W > Mo > Fe, which is similar to those of reported carbonyl octahedral complexes.[30]

^1H NMR Spectra

The ^1H NMR spectra of complexes **1**, **2**, **3**, and **4** have been assigned by comparison with those of the free ligand. An important observation is the downfield shift of the diphenylphosphine protons by 0.2–0.3 ppm. This may be ascribed to the coordination of diphenylphosphine-P to the metal center. The $SiMe_2$ protons experience a small perturbation and the chemical shift data are similar to those of the free ligand data. The CH_2 proton appears as a singlet at *ca.*1.2 ppm lower frequency to that of the free ligand (1.4 ppm). The presence of singlet peak and absence of phosphorus-hydrogen coupling clearly indicates that all the $SiMe_2CH_2PPh_2$ groups lie in the same chemical environment.

$^{31}P\{^1H\}$ NMR Spectra

The $^{31}P\{^1H\}$ NMR spectra of complexes **1**, **2**, **3** and **4** at room temperature display sharp singlets at δ 0.6, 3.8, 4.1, and 12.5 ppm, respectively, indicating that the three phosphorus atoms are equivalent.[31] The observed chemical shifts are typical for coordinated phosphorus of this type.[24] The shifts upon coordination are 18.0, 21.2, 21.5, and 30.0 ppm for **1**, **2**, **3**, and **4** respectively (δ P for ligand is –17.4 ppm). Thus, ^{31}P NMR spectra confirm the tridentate monometallic bonding of the tripodal phosphine ligand.

Cyclic Voltammetry

The electrochemical properties of the complexes **1**, **2**, **3**, and **4** were investigated by cyclic voltammetry (CV) in 0.1 M $[NBu_4][ClO_4]$ or CH_3CN solution with 100–500 mV/s scan rates. All CV data were collected under a nitrogen atmosphere and potentials were reported with reference to $Ag/0.1MAgNO_3$. All of the complexes show one oxidation ($E^{\circ/}$ −1.217 (**1**), –1.218 (**2**), −1.166 (**3**), and −1.258 (**4**) V) and one reduction ($E^{\circ/}$ .292 (**1**), 0.170 (**2**), −0.331 (**3**), and 0.338 (**4**) V), both quasireversible in nature (Table 1, Figure 1). By analogy with similar carbonyl complexes we suggest that the oxidation is primarily a metal-centered electron extraction.[32–34] In every case one quasireversible oxidation ($M^0 \rightarrow M^+$) is observed. The peak separation, ΔE_p, varies as a function of scan rates which

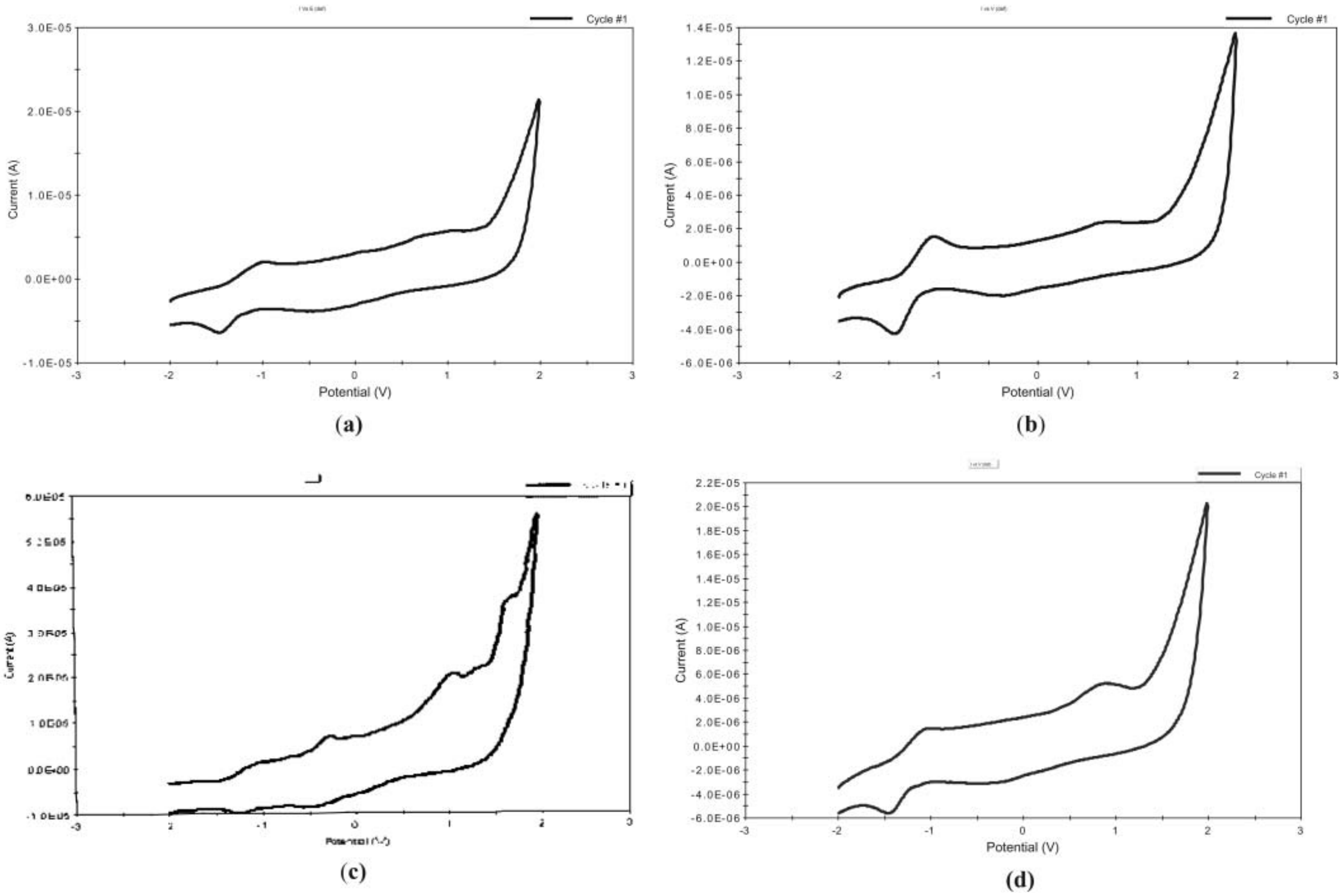
TABLE 1

Cyclic Voltammetric data[a] of a 0.1 mM solution of $[M(CO)_3\{(Ph_2PCH_2Me_2Si)_3CH\}]$ (**1**-**4**) in CH_3CN/0.1 M NBu_4ClO_4 at a glassy carbon electrode *vs* Ag/0.1 M $AgNO_3$ at different scan rates

Complex	Scan Rate	E_{pa} V(1) (i_{pa})/μA	E_{pc} V(1) (i_{pc})/μA	$E^{O/}$(1) V	ΔE_p *mV*	E_{pa}/ V(2) (i_{pa})/μA	E_{pc}/ V(2) (i_{pc})/μA	$E^{O/}$(2)/V	ΔE_p/ mV
1	100	–1.064 (0.839)	–1.408 (–4.056)	–1.236	344	0.736 (2.356)	–0.384 (–1.684)	0.176	1120
	200	–1.008 (1.208)	–1.424 (–5.812)	–1.216	416	0.748 (4.125)	–0.408 (–3.045)	0.170	1156
	300	–0.984 (2.138)	–1.464 (–7.141)	–1.224	480	0.856 (6.155)	–0.280 (–4.372)	0.288	1136
	400	–0.952 (2.638)	–1.456 (–8.392)	–1.204	504	1.248 (9.115)	–0.384 (–5.004)	0.432	1632
	500	–920 (3.535)	1.496 (–9.683)	–1.208	576	1.224 (11.620)	–0.432 (–6.215)	0.396	1656
2	100	–1.072 (1.210)	–1.408 (–3.578)	–1.240	336	0.672 (1.592)	–0.336 (–1.348)	0.168	1008
	200	–1.024 (1.503)	–1.424 (–4.292)	–1.224	400	0.656 (2.347)	–0.312 (–2.029)	0.172	968
	300	–0.984 (2.515)	–1.472 (–6.063)	–1.228	488	0.736 (4.256)	–0.376 (–3.713)	0.180	1112
	400	–0.928 (3.430)	–1.480 (–7.124)	–1.204	552	0.848 (6.190)	–0.472 (–4.734)	0.188	1320
	500	–0.920 (3.980)	1.472 (–8.065)	–1.196	552	0.728 (6.747)	–0.448 (–5.267)	0.140	1176
3	100	–1.088 (0.151)	–1.232 (–4.912)	–1.160	144	–0.104 (3.987)	–0.424 (–4.233)	–0.264	320
	200	–1.088 (0.548)	–1.224 (–8.519)	–1.156	136	–0.296 (5.671)	–0.456 (–7.750)	–0.376	160
	300	–1.120 (0.913)	–1.232 (–11.180)	–1.176	112	–0.248 (8.044)	–0.480 (–9.904)	–0.364	232
	400	–1.096 (1.493)	–1.280 (–13.460)	–1.188	184	–0.224 (10.140)	–0.432 (–11.340)	–0.328	208
	500	–1.072 (2.255)	1.232 (–15.780)	–1.152	160	–0.232 (12.260)	–0.416 (–12.860)	–0.324	184
4	100	–1.048 (0.559)	–1.432 (–3.988)	–1.240	384	0.824 (3.448)	–0.322 (–1.658)	0.251	–1146
	200	–1.064 (1.370)	–1.456 (–5.639)	–1.260	392	0.896 (5.223)	–0.360 (–3.115)	0.268	–1256
	300	–1.048) (1.676)	–1.472 (–6.768)	–1.260	424	1.032 (7.615)	–0.384 (–3.995)	0.324	–1416
	400	–1.072 (2.085)	–1.456 (–8.364)	–1.264	384	1.072 (10.09)	–0.352 (–5.123)	0.360	–1424
	500	–1.072 (2.464)	– 1.464 (–9.615)	–1.268	392	1.312 (12.60)	–0.336 (–5.629)	0.488	–1648

[a] $E^{o/} = \frac{1}{2}\,(E_{pa} + E_{pc})$; $\Delta E_p = (E_{pa} - E_{pc})$.

further shows a quasi-reversible nature of the electrode process. The reduction reflects electron accommodation in the π^* MO of the chelated ligand. The reduction appears at a more positive potential than that of the free ligand, reflecting the stabilization of the π^* MO upon coordination. The ligand reduction is also quasi-reversible in nature and the peak separation varies as a function of scan rates. A linear plot of the cathodic peak current (i_{pc}) *versus* the square root of the scan rate ($\nu^{1/2}$) passes close to the origin, indicating that the electrode process is mainly diffusion controlled.



(a) (b) (c) (d)

FIG. 1. Cyclic Voltammograms of a 0.1 mM solution of complex **1**(a), **2**(b), **3**(c), and **4**(d) in CH_3CN/0.1 M NBu_4ClO_4 at a glassy carbon electrode versus Ag/0.1 M $AgNO_3$ at 100 mV/s scan rate.

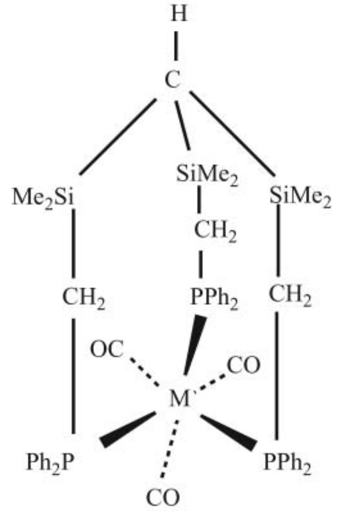


FIG. 2. Proposed structure of $[M(CO)_3\{(Ph_2PCH_2Me_2Si)_3CH\}]$ (M = Cr, Mo, W, Fe).

Efforts to grow single crystals did not succeed, and this precluded a single-crystal X-ray determination.

Proposed Structure of the Complex

The previous analytical evidence suggests an octahedral geometry around the metal with tridentate coordination of the phosphorus ligand. The proposed structure is shown in Figure 2. The carbon, silicon, and phosphorus atoms of the ligand $HC(SiMe_2CH_2PPh_2)_3$ retain their tetrahedral configuration in the complex. Similar structures have been proposed for $[M(CO)_3\{Ph_2PMe_2Si)_3CH\}]$ (M = Cr, W),[9] $[Mo(CO)_3(CyPH_2)_3]$,[35] and $[Fe(CO)_3(TPM)]$.[7]

CONCLUSION

In the present study we have demonstrated the use of tris{(diphenylphosphinomethyl)dimethylsilyl}methane for the synthesis of novel complexes of the type $[[M(CO)_3\{(Ph_2PCH_2Me_2Si)_3CH\}]$ (M = Cr(0)(**1**), Mo(0)(**2**), W(0)(**3**), and Fe(0)(**4**). These complexes have been synthesized and characterized by different spectroscopic tools. The mass fragmentation pattern shows successive removal of CO, which is a characteristic pattern of this type of compound. All the complexes show 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. ^{1}H and ^{31}P NMR spectra also confirm tridentate monometallic bonding of the tripodal phosphine ligand. Cyclic voltammogram results show quasireversible metal centered oxidation, M^+/M^0 ($E^{\circ/}$ -1.217 V(**1**), -1.218 V(**2**), -1.166 V(**3**), and -1.258 V(**4**) *vs* Ag/Ag$^+$) and ligand centered reduction (0.292 V, 0.170 V, -0.331 V, and 0.338 V vs. Ag/Ag$^+$).

REFERENCES

1. Hierso, J.C.; Amardeil, R.; Bentabet, E.; Broussier, R.; Gautheron, B.; Meunier, P.; Kalck, P. *Coord. Chem. Rev.* **2003**, *236*, 143–206.
2. Levason, W; Patai, S; Hartley, F.R., editors. *The Chemistry of Organophosphorus compounds*. Wiley, New York, **1990**.
3. Mayer, H.A.; Kaska, W.C. *Chem. Rev.* **1994**, *94*, 1239–1272.
4. Avent, A.G.; Bonafoux, D.; Eaborn, C.; Gupta, S.K.; Hitchcock, P.B.; Smith, J.D. *J. Chem. Soc. Dalton Trans.* **1999**, 831–834.
5. Gupta, S.K.; Eaborn, C.; Hitchcock, P.B; Smith, J.D.; Bohra, R., editors. *Advances in Metallo-Organic Chemistry*; RBSA Publishers Jaipur, **1999**.
6. Avent, A.G.; Bonafoux, D.; Eaborn, C.; Hill, M.S.; Hitchcock, P.B.; Smith, J.D. *J. Chem. Soc. Dalton Trans.* **2000**, 2183–2190.
7. Mague, J.T.; Dessens, S.E. *J. Organomet. Chem.* **1984**, *262*, 347–358.
8. Bookham, J.L.; McFarlane, W.; Colquhoun, I.J. *J. Chem. Soc. Dalton Trans.* **1988**, 503–507.
9. Gupta, S.K.; Pandey, S. *J. Coord. Chem.* **2004** *57*, 785–790.
10. Gupta, S.K.; Kelkar, A. *Heteroatom Chem.* **2006**, *17*, 692–698.
11. Leonard, J.; Lygo, B.; Procter, G. *Advanced Practical Organic Chemistry*, 2nd edn.; Blackwell, London, **1995**.
12. Shriver, D.F.; Drezdzon, M.A. *The Manipulation of Air-Sensitive Compounds*, 2nd edn.; Wiley, New York, **1986**.
13. Armarego, V.; Perrin, D.D. *Purification of Laboratory Chemicals*, 4th edn.; Butterworth-Heinemann, Oxford, England, **1997**.
14. Geary, W.J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.
15. Ellis, J.E. *J. Organomet Chem.* **1975**, *86*, 1–56.
16. Cowley, A.H.; Kilduff, J.E.; Ebsworth, E.A. V.; Rankin, D.W. H.; Robertson, H.E.; Seip, R. *J. Chem. Soc. Dalton Trans.* **1984**, 689–693.
17. Silverstein, R.M.; Webster, F.X. *Spectrometric Identification of Organic Compounds*, 6th edn.; Wiley, Chichester, England, **2004**.
18. Uhl, W.; Pohlmann, M.; Wartchow, R. *Angew. Chem. Int. Ed. Engl.* **1988**, *37*, 961–963.
19. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th edn.; Wiley, New York, **1997**.
20. Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th edn.; Wiley, New York, **1988**.
21. Abel, E.W.; Bennett, M.A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 2323–2327.
22. Chalmers, A.A.; Lewis, J.; Whyman, R. *J. Chem. Soc.* **1967**, 1817–1820.
23. Bullit, J.G.; Cotton, F.A.; Marks, T. *Inorg. Chem.* **1972**, *11*, 671–676.
24. King, R.B.; Kapoor, P.N.; Kapoor, R.N. *Inorg. Chem.* **1971**, *10*, 1841–1850.
25. Mason, M.R.; Duff, C.M.; Jacobson, R.A.; Verkade, J.G. *Inorg. Chem.* **1992**, *31*, 2746–2755.
26. Dahlenburg, L.; Mirzaei, F. *Inorg. Chim. Acta.* **1985**, *97*, L1–L3.
27. Coles, SJ.; Edwards, P.G.; Fleming, J.S.; Hursthouse, M.B. *J. Chem. Soc. Dalton Trans.* **1995**, 1139–1145.
28. Bookham, J.L.; McFarlane, W.; Colquhoum, I.J.; Thornton-Pett, M. *J. Organomet. Chem.* **1988**, *354*, 313–323.
29. Barton, A.J.; Connolly, J.; Levason, W.; Mendia-Jalon, A.; Orchard, S.D.; Reid, G. *Polyhedron* **2000**, *19*, 1373–1379.
30. Solomon, E.I.; Lever, A.B. P. *Inorganic Electronic Structure and Spectroscopy*, Vol. II; Wiley, New York, **1999**.
31. Verkade, J.G.; Quin, L.D. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; VCH, Florida, **1987**.
32. Zanello, P. *Inorganic Electrochemistry Theory Practice and Application*; The Royal Society of Chemistry, London, **2003**.
33. Datta, P.; Sinha, C. *Polyhedron* **2007**, *26*, 2433–2439.
34. Johnson, R.; Madhani, H.; Bullock, J.P. *Inorg. Chim. Acta* **2007**, *360*, 3414–3423.
35. Driess, M.; Faulhaber, M.; Pritzkow, H. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1892–1894.