Diphenylphosphinomethanide Complexes of Chromium(II) and Samarium(III): Preparation and Characterization of the Dinuclear $[Cr\{Ph_2PC(H)PPh_2\}_2](\mu\text{-}Cl)[\mu\text{-}C(H)(PPh_2)_2][Cr\{Ph_2PC(H)PPh_2\}]$ and Mononuclear Pseudo-allylic $Sm[\eta^3\text{-}Ph_2PC(H)PPh_2]_3$

Shoukang Hao, Jae-Inh Song, Hossein Aghabozorg and Sandro Gambarotta*

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

Reaction of lithium bis(diphenylphosphino)methanide with $CrCl_2(thf)_2$ and $SmCl_3(thf)_3$ led to the formation of an unprecedented dinuclear mixed-coordination complex $[Cr\{Ph_2PC(H)PPh_2\}_2](\mu\text{-}Cl)[\mu\text{-}C(H)(PPh_2)_2][Cr\{Ph_2PC(H)PPh_2\}]$ **1** and mononuclear $Sm[\eta^3\text{-}Ph_2PC(H)PPh_2]_3$ **2**, respectively.

Three-centre allylic-like chelating ligands (monoanionic, with a three-atom bite, two donor atoms and four π-electrons) play a pivotal role[1] in the formation of supershort metal–metal contacts.[2] Chelating phosphines with a three-atom bite, such as bis(diphenylkphosphino)methane (dppm) or bis(dimethylphosphino)methane (dmpm), have also been shown to stabilize dimetallic units with short M–M contacts.[3–5] Since these ligands work as four-electron donors and given their characteristic geometry, they may be associated with the large family of the three-centre chelating ligands. The only significant variation with respect to the anionic three-centre congeners is that the electronic conjugation between the two terminal donor atoms is interrupted by the central CH_2 group. Although the electronic communication between the two P atoms might be restored *via* deprotonation of the CH_2 group, the resulting diphosphino methanide anion $[Ph_2PC(H)PPh_2]^-$ possesses six electrons, which may be delocalized over the three atoms if the two phosphorus atoms adopt an sp^2 hybridization. A literature survey shows that this ligand works as a binucleating three-centre chelating ligand in only a few cases;[6] it functions mainly as a normal mononucleating ligand with both late[7–11] and early transition metals.[12] Moreover, in all these complexes the bonding is achieved *via* the P atoms since the M–C distances are usually significantly beyond the bonding range.

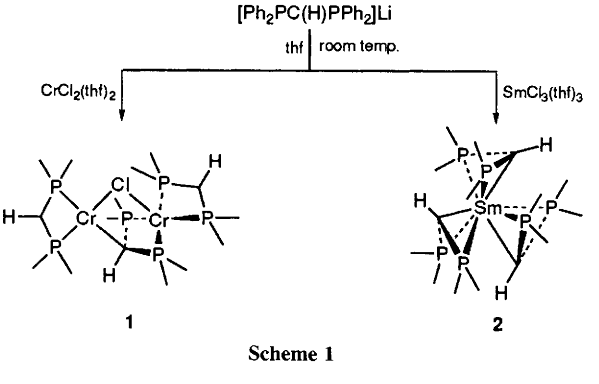
We describe the unusual structural features of the complexes formed by the reaction of $[Ph_2PC(H)PPh_2]Li$ with $CrCl_2(thf)_2$ and $SmCl_3(thf)_3$. Both reactions proceed rapidly at room temperature in thf to afford clear solutions, from which large blue crystals of dinuclear $[Cr\{Ph_2PC(H)PPh_2\}_2](\mu\text{-}Cl)[\mu\text{-}C(H)(PPh_2)_2][Cr(Ph_2PC(H)\text{-}PPh_2)]$ **1** and orange crystals of monomeric $Sm[\eta^3\text{-}Ph_2PC(H)PPh_2]_3$ **2** were obtained after solvent evaporation and recrystallization of the residual solid at room temp. from toluene–hexane mixtures (Scheme 1).†

The structure of **1**, as determined by an X-ray diffraction analysis,‡ consists of one penta- and one tetra-coordinated chromium atom (Fig. 1). The distorted square-pyramidal geometry of Cr(1) is determined by the four phosphorus atoms of two $[Ph_2PC(H)PPh_2]$ ligands which bind the basal plane [P(1)–Cr(1)–P(5) = 163.72(7), P(2)–Cr(1)–P(6) = 173.21(7)°]. The Cr(1)–P bond distances [Cr(1)–P(1) = 2.467(2), Cr(1)–P(2) = 2.468(2), Cr(1)–P(5) = 2.526(2), Cr(1)–P(6) = 2.484(2) Å] compare well with those of other Cr^{II} phosphine complexes.[3] One chlorine atom is at the apical site [Cr(1)–Cl(1) = 2.535(2) Å; P(1)–Cr(1)–Cl(1) = 105.32(7), P(6)–Cr(1)–Cl(1) = 84.24(6)°] of the square-pyramidal chromium atom, and is shared with the second square-planar chromium atom [Cr(2)–Cl(1) = 2.375(2) Å]. The other three coordination sites of the second chromium atom are occupied by the phosphorus atoms of one $Ph_2PC(H)PPh_2$ moiety [Cr(2)–P(3) = 2.462(2), Cr(2)–P(4) = 2.488(2) Å], and by the carbon atom of one of the two phosphine ligands which chelate the first chromium atom [Cr(2)–C(51) = 2.220(6) Å]. Except for this Cr–C bonding contact, all the other Cr–C distances are rather long and out of the bonding range [Cr(1)···C(1) = 3.068(2), Cr(1)···C(51) = 3.065(2), Cr(2)···C(26) = 3.101(2) Å]. The large steric bulk of the complex is apparent in the distortion of the square-planar coordination geometry of the second Cr atom [P(3)–Cr(2)–P(4) = 67.14(6), Cl(1)–Cr(2)–P(3) = 96.64(7), P(4)–Cr(2)–C(51) = 99.13(17), Cl(1)–Cr(2)–C(51) = 9.86(17)°]. One and half molecules of toluene and a disordered half molecule of thf were also found in the lattice.

The Cr–Cr distance of 3.714(1) Å is rather long and rules out any direct bonding interaction. However, the magnetic moment (μ_{eff} — 6.07 μ_B per dinuclear unit) is slightly lower than that expected for a combination of high-spin square-planar Cr^{II} and low-spin square-pyramidal Cr^{II}. Surprisingly, the complex is EPR silent in both solid state and frozen toluene solution (−200 °C).

The VIS spectrum of **1** shows one very broad absorption between 520 and 800 nm centred at 620 nm, due to superimposed $^5B_{1g}$, $^5B_{2g}$ and ^5E_g transitions of high-spin Cr^{II}.[13] A cyclic voltammogram of **1**§ showed two successive reversible one-electron reductions *ca.* −1.66 ($E_{pa} - E_{pc}$ = 76 mV) and −1.86 V ($E_{pa} - E_{pc}$ = 74 mV) *vs.* ferrocene ferrocenium (scan rate = 200 mV s^{-1}) in thf–tetrabutylammonium tetrafluoroborate ($TBABF_4$) solution at room temp., which we tentatively assign to the the reduction waves of each of the two Cr^{II} metal centres.

The crystal structure of complex **2**¶ revealed a monomeric complex with the central samarium atom nine-coordinated



Scheme 1

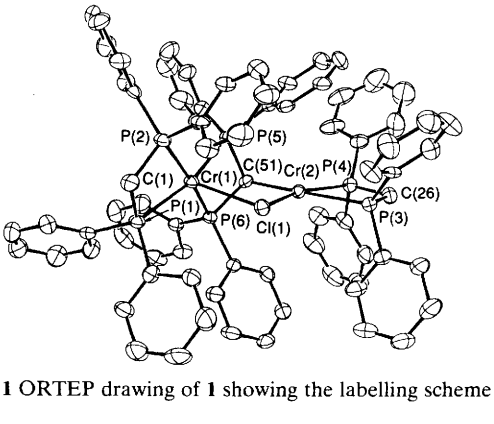


Fig. 1 ORTEP drawing of **1** showing the labelling scheme

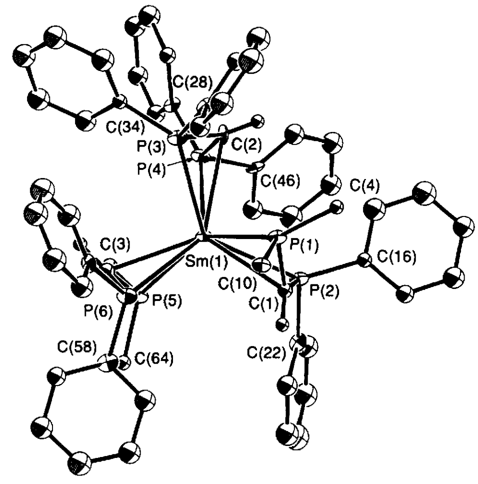


Fig. 2 ORTEP drawing of **2** showing the labelling scheme; some of the phenyl rings have been omitted for clarity

(Fig. 2) to three identical diphosphinomethanide ligands. The samarium atom is bound side-on with respect to each plane defined by the two phosphorus and bridging carbon atoms of each diphosphinomethanide molecule [Sm(1)-C(1) = 2.787(9), Sm(1)-C(2) = 2.756(9), Sm(1)-C(3) = 2.720(9), Sm(1)-P(1) = 2.857(2), Sm(1)-P(2) - 2.845(3), Sm(1)-P(3) - 2.818(3), Sm(1)-P(4) = 2.903 Å], thus resulting in a curious allylic-like bonding mode.[14] All the other bond distances and angles are comparable.

In spite of the rather symmetric side-on bonding mode, closely reminiscent of the allylic systems, the orientation of the phenyl rings defines a tetrahedral coordination geometry for the two phosphorus atoms indicating an sp^3 hybridization of the phosphorus atoms, which rules out the presence of a π system. Although complex **2** is paramagnetic with a magnetic moment $\mu_{eff} = 1.77\ \mu_B$, which is rather high for an f^5 Sm^{III} atom, it shows a well-solved ^1H NMR spectrum with the expected δ values for the resonances of the aromatic and methanide protons.†

This work was supported by the NSERC (Canada) (operating grant).

Received, 27th August 1993; Com. 3/05184F

Footnotes

† Preparation of **1**: solid $Li[Ph_2PC(H)PPh_2]$ (3.576g, 9.1 mmol) was added to a suspension of $CrCl_2(thf)_2$ (1.18g, 4.4 mmol) in thf (60 ml) under a nitrogen atmosphere at room temp. After stirring for 30 min, the solvent was evaporated *in vacuo*. The residual solid was redisolved in toluene (90 ml) and insoluble material filtered out from the hot solution. Large deep-blue crystals of **1** (2.0 g, 1.5 mmol, 68%) were obtained from solution after 5 d at room temp. IR (KBr, Nujol) ν/cm^{-1} 1583w, 1432s, 1301w, 1114m, 1094m, 1024m, 887s, 827w, 772m, 738s, 694s, 558s, 507s, 481w.

Preparation of **2**: a colourless solution of $SmCl_3(thf)_3$ (2.6 g, 5.5 mmol) in thf (100 ml) turned light orange upon treatment with solid $Li[Ph_2PC(H)PPh_2]$ (4.4 g, 11.3 mmol) at room temp. The solvent was removed *in vacuo* and the residual solid redissolved in toluene (70 ml). After removal of the insoluble material by filtration, the solution was concentrated to small volume and layered with hexane. Red–brown crystals of **2** (3.0 g, 2.3 mmol, 42%) were obtained at room temp. after 2 d. IR (KBr, Nujol) ν/cm^{-1} 1583w, 1570w, 1477m, 1432s, 1324w, 1301w, 1260w, 1180w, 1154w, 1092m, 1066w, 1025m, 999w, 911w, 865s, 775w, 736s, 694s, 648w, 616w, 603w, 513m, 485m, 470m; ^1H NMR (200 MHz, C_6D_6, 25 °C) δ 9.00 (C–H methanide), 7.18, 6.70 (m, phenyl).

‡ *Crystal data* for **1**: 1.5 $C_{75}H_{63}P_6Cr_2Cl\cdot0.5C_4H_8OC_7H_8$, M = 1466.90, monoclinic $C2/c$, a = 29.968(12), b = 22.445(12), c = 22.832(4) Å, β = 94.20(3)°, V = 15317(11) $Å^3$, Z = 8, R = 0.065, R_w = 0.064, goodness of fit = 4.05, for 754 parameters and 8032 reflections out of 13459. Data were collected at −153 °C for a crystal mounted on a glass fibre, using a Rigaku AFC6R diffractometer with graphite monochromated Mo-Kα radiation. Cell dimensions were obtained from 24 reflections in the range $40.00 \leq 2\theta \leq 50°$. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were introduced at their calculate positions but not refined. 1.5 Molecules of toluene and 0.5 molecules of thf were found in the lattice.

§ Cyclic voltammetry was performed in a N_2-filled dry-box with a EG & G cell equipped with a 0.1 mm cross-section Pt-wire as working electrode, a 5 mm long identical Pt wire as a counter-electrode, and a PAR 273 potentiostat-galvanostat (scan rate of 200 mV s^{-1}). A Pt wire electrode was used as a pseudo-reference in this experiment and potentials were referred to the ferrocene–ferrocenium potential obtained under identical conditions. Solutions were 0.01 mol dm^{-3} of parent compound in 0.3 mol dm^{-3} $TBABF_4$–THF solutions.

¶ *Crystal data* for **2**: $C_{75}H_{63}P_6Sm$, M = 1300.56, triclinic, $P\bar{1}$, a = 13.331(4), b = 21.860(8), c = 12.524(3) Å, α = 97.58(3), β = 94.20(2), γ = 75.69(3)°, V = 3159(4) $Å^3$, Z = 2, R = 0.048, R_w = 0.067, goodness of fit = 3.82, for 404 parameters and 3833 reflections out of 4530. Data were collected at −160 °C for a deep orange crystal mounted on a glass fiber, using a Rigaku AFC6R diffractometer with graphite monochromated Mo-Kα radiation. Cell dimensions were obtained from 24 reflections in the range $25.88 \leq 2\theta \leq 29.89°$. Not all the non-hydrogen atoms were anisotropically refined due to the unfavourable observation to parameter ratio. Hydrogen atoms were introduced at their calculated positions but not refined.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 S. Hao, S. Gambarotta, C. Bensimon and J. J. H. Edema, *Inorg. Chim. Acta*, 1993, **213**, 65; J. J. H. Edema and S. Gambarotta, *Comments Inorg. Chem.*, 1991, **11**, 195; J. J. H. Edema, S. Gambarotta, A. Meetsma, A. L. Spek, W. J. J. Smeets and M. Y. Chiang, *J. Chem. Soc., Dalton Trans.*, 1993, 789.

2 F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Wiley, New York, 1982; F. A. Cotton and R. A. Walton, *Metal–Metal Multiple Bonds in Dinuclear Clusters, Structure and Bonding*, Berlin, 1985, vol. 62, p. 1.

3 F. A. Cotton, R. L. Luck and K.-A. Son, *Inorg. Chim. Acta*, 1990, **168**, 3.

4 I. Ara, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 1993, **32**, 2958.

5 L. Monojlovic-Muir, K. W. Muir, I. Treurnich and R. Puddephatt, *Inorg. Chem.*, 1987, **26**, 2418.

6 H. Schmidbaur and J. R. Mandl, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 640.

7 R. Puddephatt, *Chem. Soc. Rev.*, 1983, **12**, 99.

8 V. Riera, J. Ruiz, X. Solans and E. Tauler, *J. Chem. Soc., Dalton Trans.*, 1990, 1607; V. Riera and J. Ruiz, *J. Organomet. Chem.*, 1986, **310**, C36; G. M. Dawkins, M. Green, J. C. Jeffery, C. Sambale and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 499.

9 J. M. Bassett, J. R. Maudle and H. Schmidbaur, *Chem. Ber.*, 1980, **113**, 1145; H. Schmidbaur and J. R. Mandle, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 640; K. Issleib, H. P. Abicht and H. Winkelmann, *Z. Anorg. Allg. Chem.*, 1972, **388**, 89; K. Issleib and H. P. Abicht, *J. Prakt Chem.*, 1970, **312**, 456.

10 J. A-Jibori and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 286; J. Browning, G. W. Bushned and K. R. Dixon, *J. Organomet. Chem.*, 1980, **198**, C11.

11 J. Al-Jibori and B. L. Shaw, *J. Organomet. Chem.*, 1984, **272**, 213; R. Uson, A. Laguna, M. Laguna, B. R. Manzano, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 839; J. Al-Jibori, M. Hall, A. T. Huton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1984, 863; J. Al-Jibori and B. L. Shaw, *Inorg. Chim. Acta*, 1983, **74**, 235.

12 J. J. H. Edema, A. Meetsma, F. van Bolhuis and S. Gambarotta, *Inorg. Chem.*, 1991, **30**, 2056.

13 L. F. Larkworthy, K. B. Nolan and P. O'Brien, *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon Press, Oxford, 1987, vol. 3, pp. 718–720; W. Scidel and P. Schol, *Z. Chem.*, 1978, **18**, 149.

14 M. D. Fryzuk, T. S. Haddad and D. J. Berg, *Coord. Chem. Rev.*, 1990, **99**, 137.