

Preliminary communication

Organomercuration of the carbanion derived
from $[M(CO)_4(Ph_2PCH_2PPh_2)]$ ($M = Cr, Mo$ or W).
Crystal and molecular structure of $[Cr(CO)_4\{Ph_2PCH(HgMe)PPh_2\}]$

Alan T. Hutton^{*}, Francois P. Wewers

Department of Chemistry, University of Cape Town, Rondebosch 7700, South Africa

Received 2 December 1994

Abstract

The carbanions resulting from the deprotonation by $nBuLi$ of compounds of the type $[M(CO)_4(Ph_2PCH_2PPh_2)]$ ($M = Cr, Mo$ or W) are readily organomercurated by $RHgCl$ [$R = e.g. Me, Et, Ph$, or $(C_5H_5)Fe(C_5H_5)$] to give neutral complexes of the type $[M(CO)_4\{Ph_2PCH(HgR)PPh_2\}]$. The X-ray crystal structure of the complex with $M = Cr$ and $R = Me$ has been determined, and reveals intermolecular $C-H \cdots O$ hydrogen bonding interactions to carbonyl oxygen acceptor atoms and a weak secondary intermolecular interaction between a carbonyl oxygen and the mercury atom.

Keywords: Chromium; Molybdenum; Tungsten; Carbonyl; Bis(diphenylphosphino)methane; Carbanions

Bis(diphenylphosphino)methane (dppm) is now established as an important and versatile ligand in coordination and organometallic chemistry [1]. The corresponding anion, $[Ph_2PCHPPh_2]^-$, obtained by deprotonation with a strong base such as n -butyllithium, is known to act as either a bidentate or terdentate ligand [1]. In the terdentate bonding mode the carbon atom as well as the phosphorus atoms are coordinated [1,2], whereas in the bidentate mode the anion is ambidentate: usually P,P bonding is observed [1], but there are examples of P,C bonding [3], and there is also an example of monodentate C bonding, in $[Hg\{CH(PPh_2)_2\}_2]$ [4].

In view of the ambidentate nature of the dppm anion, we thought it possible that when the neutral ligand was coordinated to a metal through both phosphorus atoms deprotonation would give a carbanion which would not be ambidentate and would be metalated selectively at carbon. We chose to study the deprotonation and subsequent organomercuration of dppm in the substituted Group 6 metal(0) carbonyls of the type $[M(CO)_4(Ph_2PCH_2PPh_2)]$ ($M = Cr, Mo$ or W). It has been shown that these are readily depro-

nated by a strong base and the resultant anion $[M(CO)_4(Ph_2PCH^-PPh_2)]$ can be alkylated or acylated by organic electrophiles to give a range of compounds of the type $[M(CO)_4(Ph_2PCHR'PPh_2)]$ ($R' = e.g. Me, Et, CH_2Ph, CH_2CH=CH_2$ or $COAr$) [5].

We now report that treatment of $[M(CO)_4(Ph_2PCH_2PPh_2)]$ ($M = Cr, Mo$ or W) with $nBuLi$ in tetrahydrofuran (THF), followed by addition of an organomercury(II) chloride $RHgCl$ ($R = Me, Et$ or Ph), results in good yields (60–80%) of the yellow, crystalline, neutral heterobimetallic complexes $[M(CO)_4\{Ph_2PCH(HgR)PPh_2\}]$, in which the carbanion formed in the deprotonation of the complexed dppm has been organomercurated.¹

All the new compounds $[M(CO)_4\{Ph_2PCH(HgR)PPh_2\}]$ ($M = Cr, Mo$ or W ; $R = Me, Et$ or Ph) gave satisfactory elemental microanalyses and were further

¹ As a general procedure, a solution of $nBuLi$ in hexane (1.5 mmol; 0.93 cm^3 of 1.6 mol dm^{-3}) was added to a solution of $[M(CO)_4(dppm)]$ (1.0 mmol) in THF (15 cm^3) at ca. 0°C . The solution was stirred for ca. 2 h and $RHgCl$ (ca. 1.4 mmol) was then added as a solid. The resulting mixture was allowed to warm to room temperature and stirred for a further 2 h. The THF was removed under reduced pressure and the residue recrystallized from dichloromethane–methanol.

^{*} Corresponding author.

characterized by their IR and ^1H and ^{31}P NMR spectra. Particularly interesting in the methylmercury complexes was the unusually high-field resonance of the methyl protons. For example, in the tungsten complex we found $\delta_{\text{H}}(200 \text{ MHz, CDCl}_3) = -0.13 \text{ ppm}$, $^2J(\text{H}-^{199}\text{Hg}) = 142 \text{ Hz}$, compared with the parent compound MeHgCl at $\delta_{\text{H}} = 1.11 \text{ ppm}$, $^2J(\text{H}-^{199}\text{Hg}) = 205 \text{ Hz}$. This is doubtless a result of the shielding effect of the dppm phenyl rings on the methyl protons (at least in the solid state structure, vide infra, phenyl rings of the dppm flank the methyl group on either side), while the difference in coupling constants is as expected when the largely ionic chloride is replaced with the covalent carbon of an electron-rich four-membered $\text{M}-\text{P}-\text{C}-\text{P}$ ring. The methanetriyl proton resonance at $\delta_{\text{H}}(\text{CDCl}_3) = 5.55 \text{ ppm}$ [triplet, $^2J(\text{H}-^{31}\text{P}) = 16 \text{ Hz}$] also shows coupling to the mercury atom [$^2J(\text{H}-^{199}\text{Hg}) \approx 118 \text{ Hz}$], but $^3J(\text{H}-^{183}\text{W})$ was not observed. The $^{31}\text{P}\{-^1\text{H}\}$ spectra gave a singlet resonance showing the expected satellites, e.g. for the complex with $\text{M} = \text{W}$ and $\text{R} = \text{Me}$ at $\delta_{\text{P}}(200 \text{ MHz, CDCl}_3, \text{ref. } 85\% \text{ H}_3\text{PO}_4) = -13.47 \text{ ppm}$ with $^1J(\text{P}-^{183}\text{W}) = 197 \text{ Hz}$ and $^2J(\text{P}-^{199}\text{Hg}) = 70 \text{ Hz}$. The latter coupling constant systematically increases in value on changing the R group on Hg, e.g. for the tungsten complex, from 52 ($\text{R} = \text{Et}$) to 70 ($\text{R} = \text{Me}$) to 81 Hz ($\text{R} = \text{Ph}$). This effect is doubtless electronic, and a result of changes in the effective nuclear charge on the Hg atom. Similar effects are observed for the corresponding parameters in the chromium and molybdenum complexes.

An X-ray crystal structure determination [9] of the methylmercury derivative $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PCH}(\text{HgMe})\text{PPh}_2)]$ (Fig. 1) revealed the expected virtually linear $\text{Me}-\text{Hg}-\text{C}(\text{chelate ring})$ geometry around mercury and an intact, almost planar $\text{Cr}-\text{P}-\text{C}-\text{P}$ chelate ring (the four torsion angles in the chelate ring are each in the range $8-10^\circ$). Although the $\text{P}-\text{C}-\text{P}$ angle in the four-membered chelate ring is $95.5(4)^\circ$, the two $\text{P}-\text{C}-\text{Hg}$ angles remain close to tetrahedral at 117° (average). Selected geometric parameters are given in the caption to Fig. 1; there are no unusual bond lengths or angles. There are, however, intermolecular close contacts from the methanetriyl $\text{C}(5)-\text{H}$ and phenyl ring $\text{C}(34)-\text{H}$ groups to carbonyl oxygen atoms on other molecules (see Table 1). Present thinking on whether such interactions can justifiably be called $\text{C}-\text{H} \cdots \text{O}$ hydrogen

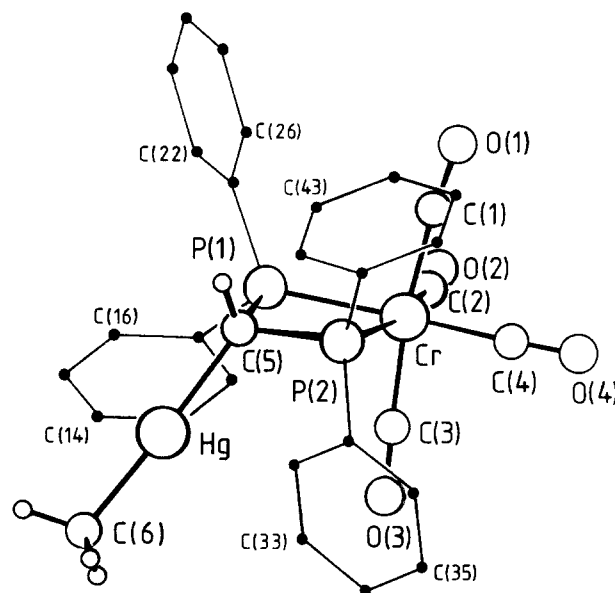


Fig. 1. Molecular structure of $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PCH}(\text{HgMe})\text{PPh}_2)]$. Selected bond distances ($\text{\AA}$): $\text{Cr}-\text{P}(1)$ 2.364(2), $\text{Cr}-\text{P}(2)$ 2.377(2), $\text{P}(1)-\text{C}(5)$ 1.834(8), $\text{P}(2)-\text{C}(5)$ 1.840(8), $\text{Hg}-\text{C}(5)$ 2.118(9), $\text{Hg}-\text{C}(6)$ 2.06(1), $\text{Cr}-\text{C}(1)$ 1.88(1), $\text{Cr}-\text{C}(2)$ 1.843(9), $\text{Cr}-\text{C}(3)$ 1.86(1), $\text{Cr}-\text{C}(4)$ 1.85(1), $\text{C}(1)-\text{O}(1)$ 1.15(1), $\text{C}(2)-\text{O}(2)$ 1.14(1), $\text{C}(3)-\text{O}(3)$ 1.19(1) and $\text{C}(4)-\text{O}(4)$ 1.16(1). Selected bond angles ($^\circ$): $\text{P}(1)-\text{Cr}-\text{P}(2)$ $70.0(1)$, $\text{P}(1)-\text{C}(5)-\text{P}(2)$ $95.6(4)$, $\text{Cr}-\text{P}(1)-\text{C}(5)$ $96.9(3)$, $\text{Cr}-\text{P}(2)-\text{C}(5)$ $96.2(3)$, $\text{C}(5)-\text{Hg}-\text{C}(6)$ $174.8(5)$, $\text{Cr}-\text{C}(1)-\text{O}(1)$ $171.8(8)$, $\text{Cr}-\text{C}(2)-\text{O}(2)$ $178.2(8)$, $\text{Cr}-\text{C}(3)-\text{O}(3)$ $177(1)$ and $\text{Cr}-\text{C}(4)-\text{O}(4)$ $177.8(9)$.

bonds indicates that the parameters presented in Table 1 do meet the current criteria for classification as hydrogen bonding interactions [10]. In addition, there is a weak secondary interaction of $3.014(8) \text{ \AA}$ between the mercury atom of the molecule at x, y, z and the carbonyl oxygen $\text{O}(2)$ of the molecule at $x-1, y, z$, the sum of the van der Waals radii for Hg ($1.55 \text{ \AA}$) and O ($1.50 \text{ \AA}$) being $3.05 \text{ \AA}$ [11]. Such weak secondary interactions, which sometimes expand the characteristic linear two-coordination favoured by mercury(II) compounds, are common, although in this case it is debatable as to whether the oxygen atom can be considered to lie within the coordination sphere of mercury [12].

The reaction reported here is quite versatile: in a search for organometallic mesogens we have synthesized by this method compounds of the type $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PCH}(\text{HgR})\text{PPh}_2)]$ where R is a long or-

Table 1
Hydrogen bonding interactions^a

$\text{C}(5) \cdots \text{O}(2)^b$	3.35(1) $\text{\AA}$	$\text{C}(34) \cdots \text{O}(4)^c$	3.37(1) $\text{\AA}$
$\text{H}(5) \cdots \text{O}(2)^b$	2.57(1) $\text{\AA}$	$\text{H}(34) \cdots \text{O}(4)^c$	2.58(1) $\text{\AA}$
$\text{C}(5)-\text{H}(5) \cdots \text{O}(2)^b$	128.7(8) $^\circ$	$\text{C}(34)-\text{H}(34) \cdots \text{O}(4)^c$	129.5(5) $^\circ$

^a Data for normalized H positions ($\text{C}-\text{H}$ bond length $1.08 \text{ \AA}$).

^b Molecule at $x-1, y, z$.

^c Molecule at $-x+1, -y, -z$.

ganic chain, e.g. $-\text{[CH}_2\text{]}_n\text{CH}_3$ ($n = 2, 7, 9$) or $-\text{C}_6\text{H}_4\text{NMeC(O)C}_6\text{H}_4\text{O[CH}_2\text{]}_n\text{CH}_3$ ($n = 1, 4, 6, 8, 11$). However, no mesogenic phases were observed. We have also fully characterized the heterotrimetallic ferrocenyl complexes $[\text{M}(\text{CO})_4(\text{Ph}_2\text{PCH}\{\text{Hg}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)\}\text{PPh}_2)]$ ($\text{M} = \text{Cr, Mo or W}$) resulting from the reaction of the anions $[\text{M}(\text{CO})_4(\text{Ph}_2\text{PCHPPH}_2)]^-$, or their lithium salts, with chloromercuriferrocene, $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)\text{HgCl}$, and are investigating their electrochemical behaviour.

In addition, the reaction can be extended to metalate the dpmm ring using metals other than mercury; for example we have obtained the yellow, crystalline, neutral chromium–gold complex $[\text{Cr}(\text{CO})_4\{\text{Ph}_2\text{PCH}(\text{AuPPh}_3)\text{PPh}_2\}]$ in good yield from the anion $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PCHPPH}_2)]^-$ and $\text{AuCl}(\text{PPh}_3)$ [13]. Further work on the metallation of the carbanions derived from these and other dpmm-containing species, using metals other than mercury, is in progress.

Acknowledgements

We thank the Foundation for Research and Development (Pretoria) and the University Research Committee of the University of Cape Town for financial support.

References and notes

- [1] R.J. Puddephatt, *Chem. Soc. Rev.*, 12 (1983) 99, and references contained therein.
- [2] E.g. R. Usón, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1984) 839; *J. Chem. Soc., Dalton Trans.*, (1985) 2417; M. Lusser and P. Peringer, *Organometallics*, 3 (1984) 1916; R. Usón, A. Laguna, M. Laguna, M.C. Gimeno, P.G. Jones, C. Fittschen and G.M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, (1986) 509.
- [3] M.P. Brown, A. Yavari, L. Manojlović-Muir and K.W. Muir, *J. Organomet. Chem.*, 256 (1983) C19; H. Schmidbaur, S. Lauteschläger and G. Müller, *J. Organomet. Chem.*, 281 (1985) 33.
- [4] M. Lusser and P. Peringer, *J. Organomet. Chem.*, 312 (1986) C61.
- [5] S. Al-Jibori and B.L. Shaw, *Inorg. Chim. Acta*, 74 (1983) 235; S. Al-Jibori, M. Hall, A.T. Hutton and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1984) 863.
- [6] A.C.T. North, D.C. Phillips and F. Scott Mathews, *Acta Crystallogr., Sect. A*, 24 (1968) 351.
- [7] G.M. Sheldrick, SHELXS-86, in G.M. Sheldrick, C. Krüger and R. Goddard (eds.), *Crystallographic Computing 3*, Oxford University Press, 1985, p. 175.
- [8] G.M. Sheldrick, SHELX-76, in H. Schenk, R. Olto-Hazenkamp, J. van Koningsveld and G.C. Bassi (eds.), *Computing in Crystallography*, Delft University Press, 1978, p. 34.
- [9] Crystal data for $\text{C}_{30}\text{H}_{24}\text{CrHgO}_4\text{P}_2$: $M = 763.05$, triclinic, space group $P\bar{1}$, $a = 8.845(2)$, $b = 11.322(2)$, $c = 15.390(3)$ Å, $\alpha = 76.92(1)^\circ$, $\beta = 86.38(2)^\circ$, $\gamma = 74.08(2)^\circ$, $V = 1444(2)$ Å³, $Z = 2$, $D_c = 1.75$ g cm⁻³, $F(000) = 740$, $\mu(\text{Mo K}\alpha) = 57.8$ cm⁻¹. 5292 reflections were measured (Enraf–Nonius CAD-4 diffractometer), of which 4783 were unique, and the 4363 with $I_{\text{rel}} > 2\sigma(I_{\text{rel}})$ were used in the analysis and refinement. An empirical absorption correction was applied [6]; transmission factors were 0.71–0.99. The structure was solved by Patterson and Fourier methods [7] and refined by full-matrix least-squares [8] with anisotropic thermal parameters for all the atoms except the H and phenyl C atoms. The H atoms were included in calculated positions and the phenyl rings were refined as rigid groups with idealized D_{6h} geometry, but with independent isotropic thermal parameters for each C atom. Final R ($= \sum |\Delta F| / \sum |F_o|$) = 0.051 and R_w ($= \sum w^{1/2} |\Delta F| / \sum w^{1/2} |F_o|$) = 0.058 [with $w = (\sigma^2 F_o + 0.0006 F_o^2)^{-1}$] for 177 variables. Tables of atom coordinates, anisotropic thermal parameters and a full list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.
- [10] R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 104 (1982) 5063; G.R. Desiraju, *Acc. Chem. Res.*, 24 (1991) 290; T. Steiner, *J. Chem. Soc., Chem. Commun.*, (1994) 2341, and references contained therein.
- [11] A. Bondi, *J. Phys. Chem.*, 68 (1964) 441.
- [12] See, e.g., N.J. Taylor, Y.S. Wong, P.C. Chieh and A.J. Carty, *J. Chem. Soc., Dalton Trans.*, (1975) 438; R.T.C. Brownlee, A.J. Canty and M.F. Mackay, *Aust. J. Chem.*, 31 (1978) 1933; A.T. Hutton, H.M.N.H. Irving, L.R. Nassimbeni and G. Gafner, *Acta Crystallogr., Sect. B*, 36 (1980) 2064, and references contained therein.
- [13] Metallation with $-\text{Au}(\text{PPh}_3)$ at the methanide carbon of cationic octahedral iron(II)–dpmm derivatives, e.g. $[\text{Fe}(\text{CNPh})_4(\text{dpmm})]^{2+}$, has been noted recently: see V. Riera, J. Ruiz, X. Solans and E. Tauler, *J. Chem. Soc., Dalton Trans.*, (1990) 1607.