DALTON
COMMUNICATION

Mercuriophosphaalkene-*P* complexes: crystal structure of [Ru{P(=CHBu^t)HgC$_5$H$_4$Fe(η-C$_5$H$_5$)}Cl$_2$(CO)(PPh$_3$)$_2$]

Anthony F. Hill,*,†,[a] Cameron Jones,*,‡,[b] Andrew J. P. White,[a] David J. Williams[a] and James D. E. T. Wilton-Ely[a]

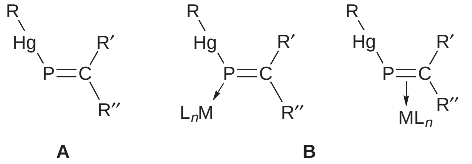
[a] *Department of Chemistry, Imperial College of Science Technology and Medicine, South Kensington, London, UK SW7 2AY*
[b] *Department of Chemistry, University of Wales, Swansea, Singleton Park, Swansea, UK SA2 8PP*

Stable complexes of mercuriophosphaalkenes have resulted from the addition of organomercury halides to the Ru–P bond of [Ru(P=CHBu^t)Cl(CA)(PPh$_3$)$_2$] (A = O or S), including the structurally characterised complex [Ru{P(=CHBu^t)HgC$_5$H$_4$-Fe(η-C$_5$H$_5$)}Cl$_2$(CO)(PPh$_3$)$_2$].

Mercury P-substituted phosphaalkenes (**A**, Scheme 1) are unknown.[1] Whilst not described prior to this work, as with so many other independently unstable molecules, co-ordination to a transition metal (**B**, Scheme 1) might be expected to confer enhanced kinetic and/or thermodynamic stability upon such molecules. The design, synthesis and structural characterisation of such compounds provide the foci for this paper. Herein we report (i) the reactions of the phosphaalkenyl complexes [Ru(P=CHBu^t)Cl(CA)(PPh$_3$)$_2$] (A = O **1a** or S **1b**) with a range of organomercury halides which result in the formation of remarkably stable complexes of mercuriophosphaalkenes: (ii) the structural characterisation of one such complex *viz.* [Ru{P(=CHBu^t)HgC$_5$H$_4$Fe(η-C$_5$H$_5$)}Cl$_2$(CO)(PPh$_3$)$_2$]. This work follows from our recent observation that complex **1a** forms an adduct with mercury(II) chloride, which was however not structurally characterised.[2]

We have recently shown that the unusual phosphaalkenyl complexes [Ru(P=CHBu^t)Cl(CA)(PPh$_3$)$_2$] (A = O **1a** or S **1b**),[2–5] result from the facile hydroruthenation of P≡CBu^t. These formally 16-electron complexes are unique in featuring an effective 1,2-dipole comprising adjacent nucleophilic phosphorus and electrophilic ruthenium centres. This reactivity is demonstrated by the 1,2 addition of ECl (E = H or AuPPh$_3$) across the ruthenium–phosphorus bond to provide the phosphaalkene complexes [Ru(EP=CHBu^t)Cl$_2$(CO)(PPh$_3$)$_2$]. It therefore appeared plausible that organomercury halides might enter into a topologically similar reaction, as indeed they do. Treating a solution of **1a** with methylmercury iodide leads to the clean formation of the complex [Ru{P(=CHBu^t)HgCH$_3$}ClI(CO)(PPh$_3$)$_2$] **2a** in high yield.§ The formulation of **2a** follows from FAB-MS and spectroscopic data amongst which the ^{31}P-{^{1}H} NMR data are immediately the most informative. The spectrum consists of two resonances; one, attributable to the chemically equivalent ruthenium bound phosphines, appears as a doublet [δ 14.9, *J*(PP) = 28.5 Hz] showing no coupling to mercury. The second resonance, in addition to being split into a triplet due to coupling to the phosphine phosphorus nuclei (δ 312.8), also shows mercury satellites [*J*(HgP) = 1358 Hz] indicating that it is to this phosphorus that the mercury is bound. The chemical shift for this resonance compares well with that for [Ru{P(=CHBu^t)AuPPh$_3$}Cl$_2$(CO)(PPh$_3$)$_2$] (δ 319.4).[4] The remaining spectroscopic data, whilst diagnostic, are unremarkable.

An analogous reaction ensues between **1a** and phenylmercury chloride to provide [Ru{P(=CHBu^t)HgPh}Cl$_2$(CO)-(PPh$_3$)$_2$] **2b**, although this results in a substantially larger ^{1}*J*(HgP) coupling in the ^{31}P NMR spectrum [δ 300.8, *J*(HgCP) = 1767 Hz]. In a similar manner the reaction of **1b** with PhHgCl provides the thiocarbonyl analogue [Ru{P(=CHBu^t)HgPh}Cl$_2$-(CS)(PPh$_3$)$_2$] **2c** (Scheme 2). Chloromercurioferrocene also adds cleanly to **1a** and **1b** to provide [Ru{P(=CHBu^t)HgC$_5$H$_4$Fe(η-C$_5$H$_5$)}Cl$_2$(CA)(PPh$_3$)$_2$] (A = O **2d** or S **2e**). In the case of **2d** crystals suitable for crystallographic analysis were obtained¶



Scheme 1

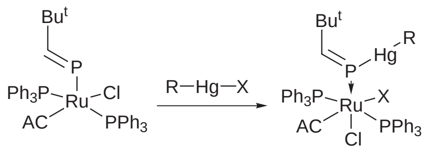
---

† E-Mail: a.hill@ic.ac.uk

‡ E-Mail: c.a.jones@swansea.ac.uk

§ Selected data for new complexes [25 °C, IR (Nujol), NMR (CDCl$_3$, 25 °C), FAB-MS (nitrobenzyl alcohol)]. Syntheses were carried out in dichloromethane at room temperature, monitoring the reaction progress by FT-IR spectroscopy (typically 1–3 h) using 0.2 mmol of each reagent. **2a**: IR 1965 [ν(CO)] cm^{-1}. NMR: ^{1}H δ 0.41 [d, 3 H, HgCH$_3$, *J*(PH) = 4.7], 0.87 (s, 9 H, Bu^t), 7.51 [d, P=CH, *J*(PC) = 5.9 Hz], 7.31, 7.93 [m × 2, 30 H, C$_6$H$_5$]; ^{13}C-{^{1}H} δ 198.8 (m, RuCO), 180.2 [d, P=CH, *J*(PC) = 14.0], 135.3–127.8 (C$_6$H$_5$), 41.1 [d, P=CH*C*, *J*(PC) = 10.8], 31.3 [d, C*C*H$_3$, *J*(PC) = 11.9], 15.2 [d, HgC, *J*(PC) = 56.1 Hz]; ^{31}P-{^{1}H} δ 312.8 [t, HgP, *J*(PP$_2$) 28.5, *J*(HgP) 1358], 14.9 [d, RuPPh$_3$, *J*(PP) = 28.5 Hz]. FAB-MS: *m*/*z* 1007 (15) [*M* − I]$^+$, 781 (12) [*M* − Cl − MeHgP=CHBu^t]$^+$, 755 (100%) [M − Cl − CH$_3$HgI]$^+$. **2b**: IR 1976, 1965 (sh) [ν(CO)] cm^{-1}. NMR: ^{1}H δ 0.90 (s, 9 H, Bu^t), 7.13–7.97 (m × 4, 36 H, P=CH + C$_6$H$_5$); ^{31}P-{^{1}H} δ 300.8 [t, RuHgP=CH, *J*(PP$_2$) 28.5, *J*(HgCP) 1767], 19.0 [d, RuPPh$_3$, *J*(PP$_2$) = 28.5 Hz]. FAB-MS: *m*/*z* 1067 (5) [*M* − Cl]$^+$, 1027 (2) [*M* − Ph]$^+$, 755 (11%) [*M* − Cl − PhHgCl]$^+$. **2c**: IR 1289 [ν(CS)] cm^{-1}. NMR: ^{1}H δ 0.91 (s, 9 H, CH$_3$), 7.25, 8.00 (m × 2, 35 H, C$_6$H$_5$), 7.67 [d, 1 H, P=CH, *J*(PH) = 7.7 Hz]; ^{31}P-{^{1}H} δ 292.8 [t, RuHgP=CH, *J*(PP) = 27.7, *J*(HgP) = 1801], 19.9 [RuPPh$_3$, *J*(PP) = 27.7 Hz]. FAB-MS: *m*/*z* 1119 (7) [*M*]$^+$, 1084 (10) [*M* − Cl]$^+$, 807 (9) [*M* − PhHgCl]$^+$, 771 (62%) [*M* − Cl − PhHgCl]$^+$. **2d**: IR 1976, 1960 (sh) [ν(CO)] cm^{-1}. NMR: ^{1}H δ 0.89 [d, 9 H, Bu^t, *J*(PH) = 1.2], 3.86, 4.34 [pseudo-t × 2, 2 H × 2, *J*(HH) = 1.6 Hz], 4.12 (s, 5 H, C$_5$H$_5$), 7.37–7.98 [m × 4, 31 H, P=CH + C$_6$H$_5$]; ^{13}C-{^{1}H} δ 198.5 (m, RuCO), 181.5 [d, P=CH, *J*(PC) = 18.3], 134.8–128.0 (C$_6$H$_5$), 98.8 [d, HgC, *J*(PC) = 76.6], 73.9 [d, C^{2,5}(C$_5$H$_4$), *J*(PC) = 5.2], 69.6 [d, C^{3,4}(C$_5$H$_4$), *J*(PC) = 4.3], 68.3 (C$_5$H$_5$), 41.3 [d, P=CH*C*, *J*(PC) = 11.9], 31.4 [d, CH$_3$, *J*(PC) = 12.9 Hz]; ^{31}P-{^{1}H} δ 300.4 [t, RuHgP=CH, *J*(PP$_2$) 29.3, *J*(HgCP) 1943], 19.7 [d, RuPPh$_3$, *J*(PP) = 29.3 Hz]. FAB-MS: *m*/*z* 1209 (5) [*M*]$^+$, 1173 (8) [*M* − Cl]$^+$, 755 (19%) [*M* − Cl − CpFeC$_5$H$_4$HgCl]$^+$.

¶ Crystal data for **2d**: C$_{52}$H$_{49}$Cl$_2$FeHgOP$_3$Ru, *M* = 1211.1, monoclinic, space group $P2_1/c$ (no. 14), a = 20.889(2), b = 11.893(1), c = 19.544(3) Å, β = 99.40(1)°, U = 4790.3(9) Å^3, Z = 4, μ(Mo-Kα) = 40.6 cm^{-1}. 8346 Independent reflections were measured to give $R1$ = 0.070, and $wR2$ = 0.132 [4513 observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 50°$] and 478 parameters. CCDC reference number 186/937. http://www.rsc.org/suppdata/dt/1998/1419/ for crystallographic files in .cit format.



	A
1a	O
1b	S

	A	X	R
2a	O	I	CH_3
2b	O	Cl	Ph
2c	S	Cl	Ph
2d	O	Cl	$C_5H_4Fe(\eta\text{-}C_5H_5)$
2e	S	Cl	$C_5H_4Fe(\eta\text{-}C_5H_5)$

Scheme 2

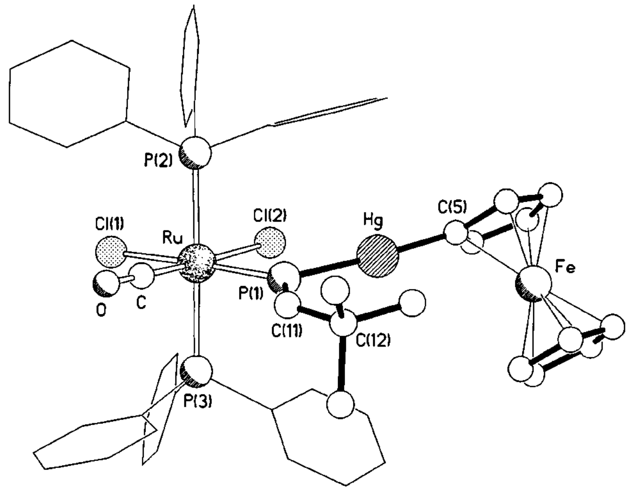


Fig. 1 Molecular structure of complex **2d**. Hydrogen atoms omitted and phenyl groups simplified

and were established to have the *cis*-$RuCl_2$ structure depicted in Fig. 1.

The geometry at ruthenium is distorted octahedral with *cis* inter-ligand angles in the range 84.10(14)–93.9(2)°. The two *cis* Ru–Cl bonds at 2.454(4) and 2.469(4) Å are of identical length indicating comparable *trans* influences for the carbonyl and phosphaalkene ligands. The plane defined by the atoms Hg, P(1), C(11) and C(12) of the phosphaalkene ligand is twisted by only 7° from the equatorial co-ordination plane. The key geometrical features of the phosphaalkene include: (i) a dramatically shortened (32σ) Ru–P(1) bond length of 2.277(4) Å relative to the ruthenium phosphine bond lengths of Ru–P(2) [2.405(4)] and Ru–P(3) [2.416(4) Å]; (ii) trigonal co-ordination at P(1) [angle sum 360.0°]; (iii) a short P(1)–C(11) bond length of 1.69(2) Å reflecting marked multiple bond character; and (iv) a short P(1)–Hg bond length of 2.377(4) Å. Being the first structurally characterised Hg–P(sp^2) bond length, no precedent for comparison exists, however it is clearly short relative to the very few examples reported for bonds between mercury and three-co-ordinate pyramidal phosphorus, *e.g.* 2.402(1) in $[Hg_2\{\mu\text{-}P(SiMe_3)_2\}_2\{PSiMe_3)_2\}_2]$[6] and 2.442(3)/2.451(3) Å for $[Hg(PBu^t_2)_2]$.[7] It is notable that the non-bonded Hg–Cl(2) distance is relatively short, being less than the sum of the van der Waals radii and is accompanied by a contraction in both the P(1)–Ru–Cl(2) (84°) and Hg–P(1)–Ru (115°) angles.

The results described above illustrate the utility of terminal phosphaalkenyl ligands as precursors for complexes of metallated phosphaalkenes. The complexes **2a**–**2d** are indefinitely stable under ambient conditions, however **2e** slowly extrudes elemental mercury in solution, and the nature of this curious product is currently under investigation.

Acknowledgements

We wish to thank the Engineering and Physical Sciences Research Council (UK) and the Wolfson Foundation for financial support. A. F. H. gratefully acknowledges the award of a Senior Research Fellowship by The Royal Society and The Leverhulme Trust. Ruthenium salts were generously provided by Johnson Matthey Ltd.

References

1 For a recent review of the chemistry of phosphaalkenes see L. Weber, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 271 and refs. therein. Bickelhaupt has however reported the synthesis of C-mercurated phosphaalkenes *via* the reactions of $LiCH{=}PC_6H_2Bu^t_3$ with mercury(II) chloride: S. J. Goede, H. P. van Schaik, F. Bickelhaupt, H. Kooijamn and A. L. Spek, *Organometallics*, 1992, **11**, 3844.

2 R. B. Bedford, A. F. Hill, C. Jones, J. D. E. T. Wilton-Ely, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1997, 179.

3 R. B. Bedford, D. E. Hibbs, A. F. Hill, M. B. Hursthouse, K. M. A. Malik and C. Jones, *Chem. Commun.*, 1996, 1895.

4 R. B. Bedford, A. F. Hill and C. Jones, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 547.

5 R. B. Bedford, A. F. Hill, C. Jones, J. D. E. T. Wilton-Ely, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1997, 139, 1113.

6 S. C. Goel, M. Y. Chiang, D. J. Rauscher and W. E. Buhro, *J. Am. Chem. Soc.*, 1993, **115**, 160.

7 B. L. Benac, A. H. Cowley, R. A. Jones, C. M. Nunn and T. C. Wright, *J. Am. Chem. Soc.*, 1989, **111**, 4986.

Received 23rd *February* 1998; *Communication* 8/01513I