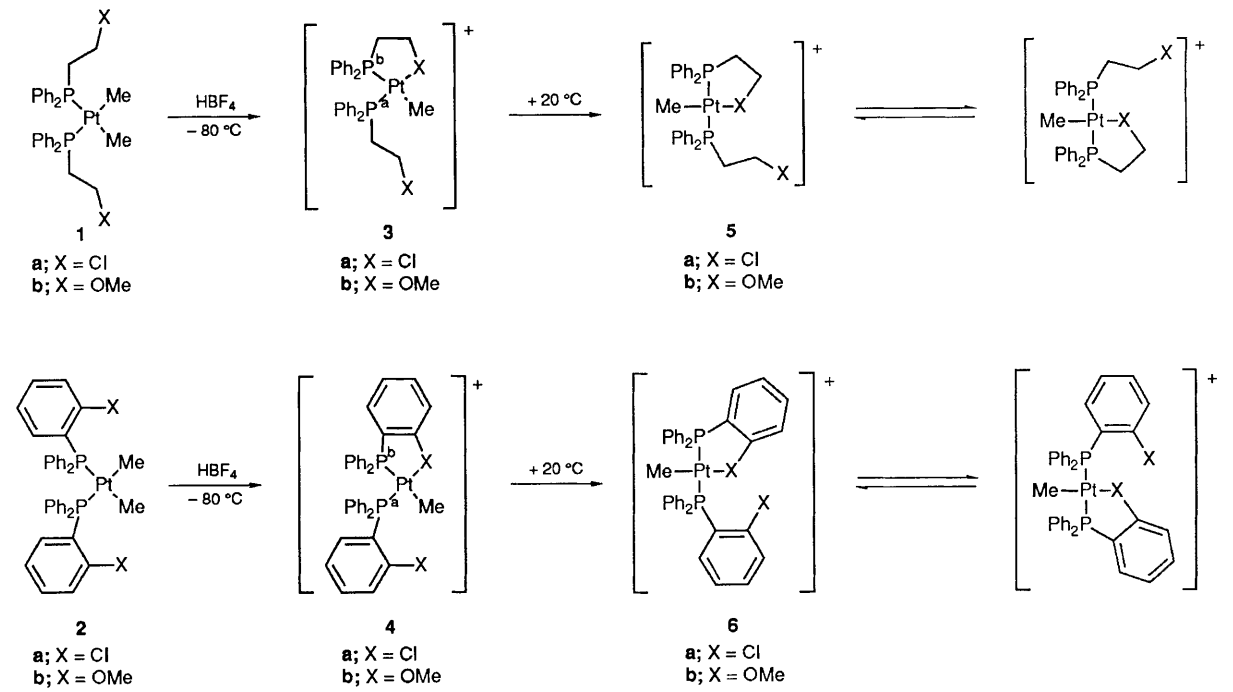
Halocarbon Complexes of Platinum(II)

Tania M. Gomes-Carneiro, Richard D. Jackson, Joanne H. Downing, A. Guy Orpen and Paul G. Pringle*
School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

Chelate-stabilised halocarbon–platinum(II) complexes of the general type *cis*- and *trans*-[MePt(η^2-Ph_2PY)(η^1-Ph_2PY)][BF_4] where Y = CH_2CH_2Cl, *o*-C_6H_4Cl or *o*-$CH_2C_6H_4X$, X = Cl, Br or I, are reported and the relative *trans*-influence of the halocarbon donors is discussed; the X-ray crystal structures of [MePt(η^2-$Ph_2PCH_2CH_2Cl$)(η^1-$Ph_2PCH_2CH_2Cl$)][BF_4] and [MePt{η^2-Ph_2P(*o*-C_6H_4Cl)}{η^1-Ph_2P(*o*-C_6H_4Cl)}][BF_4] have been determined.

The isolation of stable halocarbon complexes of several transition metals has dispelled the belief that halocarbons are non-coordinating solvents and raised the possibility that halocarbon complexes may be intermediates in oxidative addition reactions.[1–5] Halocarbon solvents are routinely used in platinum(II) chemistry and oxidative addition of halocarbons to platinum(II) has been widely studied.[6] Furthermore, theoretical studies[7] suggest that halocarbon–platinum(II) complexes are involved in some oxidative additions but, to date, no halocarbon complexes of platinum have been reported.[1] As part of a study[8] of weakly protected d^8-PtL_2 and d^8-PtL_3 fragments, we have made such complexes and addressed the question of the relative *trans*-influence of halocarbons donors at platinum(II) as a measure of the halocarbon ligation.



Scheme 1 Synthesis of chlorocarbon and ether complexes of platinum(II) and intramolecular exchange mechanism in the *trans*-chelates

Addition of HBF_4 in diethyl ether to dichloromethane solutions of the dimethyl complexes **1a** and **2a** at −80 °C gives the *cis*-complexes **3a** and **4a** respectively (see Scheme 1), as shown by their characteristic AX $^{31}P\{^1H\}$ NMR spectra (see Table 1). When the solutions of **3a** or **4a** are warmed to +20 °C the signals for the *cis*-complexes disappear and are replaced by singlets. If these solutions are then recooled to −80 °C the fluxionality is arrested and the $^{31}P\{^1H\}$ NMR data unambigously identify the species as the *trans*-chelates **5a** and **6a**. The unsymmetrical complexes **7** and **8** are not fluxional and thus the fluxionality of **5a** and **6a** is due to intramolecular exchange of the coordinated and non-coordinated halogen atoms (see Scheme 1); we also observe similar fluxionality in the phosphino-ether platinum(II) chelates **5b** and **6b**.

The X-ray crystal structures of **5a**[†] and **6a**[‡] (see Figs. 1 and 2) reveal that the Pt–Cl distance in **5a** is significantly shorter than in **6a**, consistent with the chloroalkane being a stronger σ-donor and having a higher *trans*-influence than the chloroarene. This conclusion is also supported by ^{13}C NMR data:[9] $^1J(PtC)$ is smaller for **5a** than **6a** (714 and 730 Hz respectively).

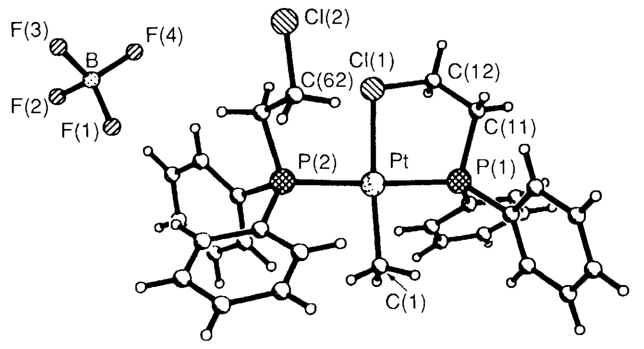


Fig. 1 Molecular structure of $[MePt(\eta^2\text{-}Ph_2PCH_2CH_2Cl)(\eta^1\text{-}Ph_2PCH_2CH_2Cl)][BF_4]$ **5a**. Selected bond distances (Å): Pt–P(1) 2.275(2), Pt–P(2) 2.309(2), Pt–Cl(1) 2.425(2), Pt–C(1) 2.050(7), C(12)–Cl(1) 1.797(7), C(62)–Cl(2) 1.755(7). Selected bond angles (°): Pt–Cl(1)–C(12) 103.4(3), Cl(1)–Pt–P(1) 91.7(1). Selected torsion angle (°): Pt–Cl(1)–C(12)–C(11) −40.0(6).

Since there is a coordinated and a non-coordinated chlorocarbon group in both **5a** and **6a** these structures are ideal for detecting any C–Cl lengthening upon coordination, as some calculations have suggested.[3] We can conclude from our structures that the lengthening of the C–Cl bond is at best small, and comparable in magnitude to librational and statistical uncertainties (see Figure captions for the data).

In order to probe the relative strength of the chlorocarbon binding to platinum(II) we have made the ether chelates **3b** and **4b** (see Scheme 1) and by comparison of the $^1J(PtP^a)$ values (see Table 1) it may be concluded that, for these five-membered rings, chloroarene and aryl alkyl ether ligands have a similar *trans*-influence whereas chloroalkane has a significantly lower *trans*-influence than dialkyl ether ligands.

The synthesis of an exactly analogous series of chlorocarbon–, bromocarbon– and iodocarbon–platinum(II) complexes has proved difficult because either the ligand has been unstable (*e.g.* $Ph_2PCH_2CH_2X$, X = Br, I) or the platinum complexes rapidly undergo oxidative additions of the ligand

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[†] *Crystal data*, **5a**: $C_{29}H_{31}BCl_2F_4P_2Pt$, M = 794.3, triclinic, space group $P\bar{1}$ (No. 2); a = 9.764(2), b = 12.348(2), c = 13.251(2) Å, α = 73.120(124), β = 83.610(16), γ = 80.26(2)°, U = 1503.5(5) Å^3, Z = 2, D_c = 1.754 g cm^{-3}, $F(000)$ = 776 electrons, μ(Mo-Kα) = 5.041 mm^{-1}, λ = 0.71069 Å. The final R is 0.034 for 4637 unique observed [$I > 2\sigma(I)$] absorption corrected reflections collected at room temperature for $4 < 2\theta < 50°$ on a Siemens R3m/V diffractometer using graphite monochromated X-radiation for a hemisphere of reciprocal space.

[‡] *Crystal data*, **6a**: $C_{37}H_{31}BCl_2F_4P_2Pt$, M = 890.4, orthorhombic, space group *Pbca* (No. 61); a = 12.625(2), b = 23.456(4), c = 23.560(4) Å, U = 6977(2) Å^3, Z = 8, D_c = 1.695 g cm^{-3}, $F(000)$ = 3488 electrons, μ(Mo-Kα) = 4.36 mm^{-1}, λ = 0.71069 Å. The final R is 0.038 for 5049 unique observed [$I > 2\sigma(I)$] absorption corrected reflections collected at −100 °C for $4 < 2\theta < 50°$ on a Siemens R3m/V diffractometer using graphite monochromated X-radiation for an octant of reciprocal space. For both structures, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

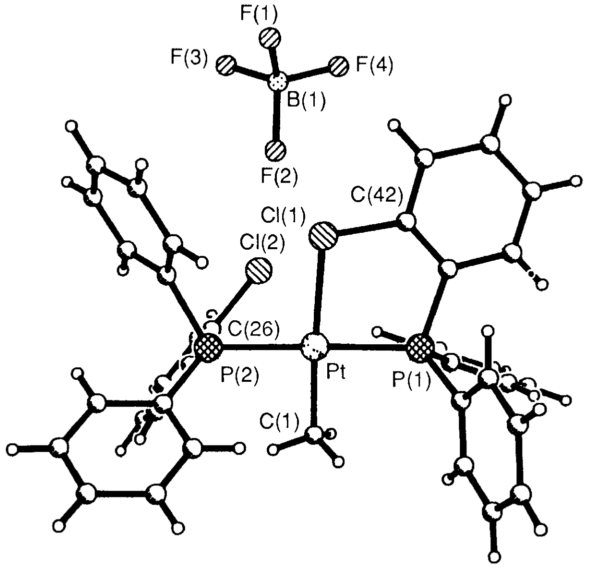
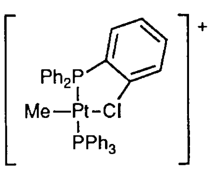


Fig. 2 Molecular structure of $[MePt\{\eta^2\text{-}Ph_2P(o\text{-}C_6H_4Cl)\}\{\eta^1\text{-}Ph_2P(o\text{-}C_6H_4Cl)\}][BF_4]$ **6a**. Selected bond distances (Å): Pt–P(1) 2.278(1), Pt–P(2) 2.310(1), Pt–Cl(1) 2.462(1), Pt–C(1) 2.053(6), C(42)–Cl(1) 1.788(5), C(26)–Cl(2) 1.764(6). Selected bond angles (°): Pt–Cl(1)–C(42) 103.9(2), Cl(1)–Pt–P(1) 86.2(1). Selected torsion angle (°): Pt–Cl(1)–C(42)–C(41) −3.2(5).



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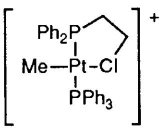

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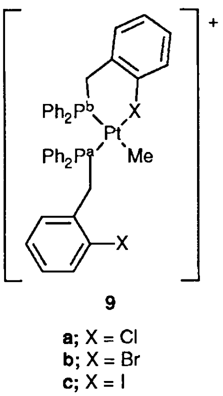

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a; X = Cl
b; X = Br
c; X = I
d; X = OMe

10 **11**

Table 1 $^{31}P\{^1H\}$ NMR data[a]

Complex	$\delta(P^a)$	$^1J(PtP^a)$/Hz	$\delta(P^b)$	$^1J(PtP^b)$/Hz
3a	9.3	4978	55.2	1914
3b	6.5	4896	49.4	1947
4a	17.1	5240	35.6	2070
4b	7.7	5249	42.1	2045
9a	15.2	5013	48.4	2141
9b	16.1	4810	44.5	2114
9c	18.2	4673	34.7	2089
9d	11.0	4820	57.0	2105

[a] All spectra measured at 36.4 MHz in CD_2Cl_2 at −80 °C; chemical shifts (± 0.1 ppm) to high frequency of 85% H_3PO_4.

(*e.g.* with $Ph_2PCH_2C_6H_4I$). However, we have characterised by $^{31}P\{^1H\}$ NMR spectroscopy at low temperature (< -60 °C) the six-membered chelate halocarbon complexes **9a–c** and the ether complex **9d** for comparison. From the ^{31}P NMR data (see Table 1) we can conclude that in the six-membered chelates **9a–d** the *trans*-influence of the halocarbon donors is in the order ArI > ArBr > ArCl and ArBr ≈ ArOMe.

Preliminary results show that the Pt–Cl bonds of the chlorocarbon donors in **5a** and **6a** are labile and can be substituted by solvents such as Me_2CO or tetrahydrofuran but *not* water. The C–Cl bonds of these species are also potentially labile as shown by the reaction of complex **5a** with Ph_2PH to give the intermediate **10** which, upon treatment with Et_3N, gives the $Ph_2PCH_2CH_2PPh_2$ (dppe) complex **11** quantitatively by an intramolecular ring closure.

We thank the SERC for support and Johnson Matthey for a generous loan of platinum.

Received, 18th October 1990; Com. 0/04694I

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