Cationic Palladium and Platinum Complexes with Diolefin Ligands †

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Chlorine-bridged complexes $[M_2(diolefin)_2Cl_2][BF_4]_2$ have been prepared from $[M(diolefin)Cl_2]$ [M = Pd or Pt; diolefin = cyclo-octa-1,5-diene (cod) or norborna-2,5-diene (nbd)] and $[Et_3O][BF_4]$. The complex $[Pd(cod)_2Cl_2][BF_4]_2$ rapidly forms 5,6-η-cyclo-oct-5-enyl complexes $[Pd_2(2\text{-}Rcot)_2Cl_2]$ (R = MeO, $MeCO_2$, or HO) with MeOH, $MeCO_2H$, or H_2O; PPh_3 displaces the cod to form $[Pd_2Cl_2(PPh_3)_4][BF_4]_2$, but the platinum analogue forms $[Pt(cod)Cl(PPh_3)][BF_4]$. Complexes $[M(diolefin)Cl(PR_3)]X$ (X = SFO_3, BF_4, or ClO_4) have been obtained from *sym,trans*-$[M_2Cl_4(PR_3)_2]$ and the diolefin with $SFO_2(OMe)$–C_6H_6, $[Et_3O][BF_4]$–CH_2Cl_2, or $Na[ClO_4]$–Me_2CO.

METHYL fluorosulphate and the trialkyloxonium tetrafluoroborates $[R_3O][BF_4]$ (R = Me or Et) abstract halide ligands from complexes of transition metals, and because the anions $[SFO_3]^-$ and $[BF_4]^-$ are poor donors towards many transition metals the complexes produced in these reactions are frequently cationic in character.[1] Since unsaturated ligands have enhanced susceptibility to nucleophilic attack in cationic complexes,[2] we have examined the utility of the alkylating agents $SFO_2(OMe)$ and $[Et_3O][BF_4]$ in the synthesis of cationic diolefin complexes of Pd^{II} and Pt^{II}.

RESULTS AND DISCUSSION

The complexes *cis*-$[MCl_2L_2]$ (M = Pd or Pt; L = phosphine) react with the alkylating agents to form salts of the chlorine-bridged cations $[M_2Cl_2L_4]^{2+}$ and we have found that the reactions between $[Et_3O][BF_4]$ and the complexes $[M(diolefin)Cl_2]$ [M = Pd or Pt; diolefin = cyclo-octa-1,5-diene (cod) or norborna-2,5-diene (nbd)]

$$2[M(diolefin)Cl_2] + 2[Et_3O][BF_4] \longrightarrow [M_2(diolefin)_2Cl_2][BF_4]_2 + 2EtCl + 2Et_2O \quad (1)$$

proceed in a similar manner [equation (1)]. The complexes $[M_2(diolefin)_2Cl_2][BF_4]_2$ (M = Pd or Pt; diolefin = cod or nbd) are thus formulated on the basis of analytical data (except for M = Pd, diolefin = nbd), conductivities in nitromethane indicative of 2 : 1 electrolytes, i.r. bands characteristic of $[BF_4]^-$, and two ν(M–Cl) bands at 365—320 and 310—340 cm^{-1}, the frequencies of which are typical of bridging chlorines in cationic complexes.[3] The complexes are air sensitive, changing from yellow to green (for Pd) or from colourless to brown (for Pt). The complex $[Pd_2(nbd)_2Cl_2][BF_4]_2$ decomposes within a few minutes in air and a satisfactory analysis was not obtained; $[Pd_2(cod)_2Cl_2][BF_4]_2$ is stable in air for a few hours. The qualitative stability orders are cod > nbd and Pt > Pd. The complexes are soluble in acetone, but not in chlorinated solvents.

Attempts to prepare cationic complexes of *endo*-dicyclopentadiene (dcpd) by the method of equation (1) resulted in decomposition and deposition of metal. Since enyl complexes derived from dcpd such as $[Pd(pd)(C_{10}H_{12}OMe)]$ (pd = pentane-2,4-dionato) have been converted into dcpd complexes by treatment with $[Ph_3C][BF_4]$,[4] we investigated the reaction between $[Pd_2(C_{10}H_{12}OMe)_2Cl_2]$ and $SFO_2(OMe)$ but were unable to obtain the cationic dcpd complex. Since even the neutral complexes $[M(dcpd)Cl_2]$ are very susceptible to nucleophilic attack,[5] the failure to obtain the much more reactive cationic complex is readily understood.

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† No reprints available.

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As expected, the susceptibility of the co-ordinated diolefins to nucleophilic attack was much greater in the cationic complexes than in [M(diolefin)Cl_2]. Whereas the uncharged complexes react only with the conjugate bases of alcohols or carboxylic acids (*e.g.*, MeOH–$Na_2[CO_3]$ [5] or Ag[O_2CMe] [6]), the complex [Pd_2(cod)$_2Cl_2$][BF_4]$_2$ reacted very rapidly with MeOH, MeCO_2H, or H_2O to form [Pd_2(2-Rcot)$_2Cl_2$] (R = MeO, MeCO_2, or HO). The 2-hydroxycyclo-oct-5-enyl complex (R = HO) is air stable, soluble in benzene and chlorinated solvents, and is a non-conductor in nitromethane. The i.r. spectrum had ν(OH) at 3 800—3 500 cm^{-1} and there was no absorption indicative of [BF_4]$^-$. The ^{1}H n.m.r. spectrum of a $CDCl_3$ solution had a multiplet at τ 4.25 (*I* = 2) from the olefinic protons, a complex region τ 6.5—7.0 (*I* = 2) from the protons on carbon substituted by Pd or OH, resonances from methylene groups τ 7.0—8.0 (*I* = 8), and a singlet at τ 8.5 (*I* = 1), assigned to the hydroxyl proton, which disappeared on addition of D_2O. The spectrum is similar to that reported for [Pd_2Br_2(2-HOcot)$_2$].[7]

A reaction between [Pt(cod)$_2Cl_2$][BF_4]$_2$ (1 mol) and PPh_3 (2 mol) in acetone formed the cationic diolefin complex [Pt(cod)Cl(PPh_3)][BF_4] in high yield. However, reaction of the corresponding palladium complex resulted in displacement of the diolefin ligand and formation of [$Pd_2Cl_2(PPh_3)_4$][BF_4]$_2$ in *ca.* 50% yield. Because the cationic complexes [M(diolefin)Cl(PR_3)][BF_4] were not available by this route for M = Pd, we employed an alternative synthesis [equation (2)] which avoids the use of free phosphines. The complexes prepared by this route or by use of SFO_2(OMe) in place

$$\textit{sym,trans}\text{-}[M_2Cl_4(PR_3)_2] + 2\ \text{diolefin} + 2[Et_3O][BF_4] \longrightarrow 2[M(\text{diolefin})Cl(PR_3)][BF_4] + 2EtCl + 2Et_2O \quad (2)$$

of [Et_3O][BF_4] are given in the Table. This method, in which chloride is removed by reaction with the alkylating agent, is analogous to the procedure adopted by Church and Mays [8] for promoting the displacement of chloride ligands by neutral donors. These workers carried out reactions in acetone in the presence of Na[ClO_4], which led to the precipitation of chloride as NaCl and the formation of perchlorate salts. We obtained [Pt(cod)Cl(PBu_3)][ClO_4] by this method (Table). Some complexes of the type [Pt(cod)Cl(PR_3)][BF_4] have been obtained previously by treatment of [Pt(2-Rcot)Cl(PR_3)] [R = CH(COMe)$_2$] with [Ph_3C][BF_4];[4] the method of equation (2) is clearly more convenient. The complexes [MCl(PR_3)(diolefin)]X are generally insoluble in organic solvents, and satisfactory n.m.r. spectra were obtained only for the more soluble complexes.

Characterisation of complexes [Pt(diolefin)Cl(PR_3)]X

					Analysis (%)							^{1}H N.m.r. (olefinic protons) [b]			
					Found		Calc.					*trans* to P		*trans* to Cl	
Diolefin	M	PR_3	X	M.p. (θ_c/°C)	C	H	C	H	Λ_M [a] S cm^2 mol^{-1}	$\bar{\nu}$(M–Cl) cm^{-1}	τ	^3J(PPtCH) Hz	^2J(PtCH) Hz	τ	^2J(PtCH) Hz
cod	Pt	PMe_2Ph	BF_4	134—135	34.2	4.2 [c]	34.1	4.1	80	321	3.82	3.0	45.0	4.6	68
cod	Pt	PPh_3	BF_4	260—265	45.6	3.6	45.4	3.9	65	345					
cod	Pt	PPh_3	SFO_3	260—262	44.2	3.9	44.6	3.9	65	345					
cod	Pt	PBu_3	ClO_4	125—126 (decomp.)	37.8	6.4	37.5	6.2	60	319	3.8	3.0	44.5	4.6	65
cod	Pd	PPh_3	BF_4	150—160	47.5	4.6 [d]	47.4	4.4	60	339	3.6	3.0		4.3	
nbd	Pt	PBu_3	SFO_3	120—122	36.5	6.0 [e]	36.6	5.6	84	323	3.75	4.25	38.5	4.2	65
nbd	Pt	PMe_2Ph	BF_4	155—188 (decomp.)	33.1	3.5	32.8	3.5	72	319	3.8	4.0	38.0	4.2	65
nbd	Pt	PPh_3	BF_4	230—240 (decomp.)	41.3	3.2	41.3	3.3	75	326					
dcpd	Pt	PMe_2Ph	BF_4	142—150 (decomp.)	36.6	4.2 [f]	36.8	3.9	85	320					

[a] From *ca.* 10^{-3} mol dm^{-3} solutions in nitromethane. [b] In $CDCl_3$. [c] Cl, 6.6 (calc., 6.3%). [d] Calculated for one molecule of CH_2Cl_2 of crystallisation; Cl, 16.1 (calc., 15.5%). [e] Cl, 5.8 (calc., 5.7%). [f] Cl, 6.8 (calc., 6.0%).

The olefinic bonds in the complexes [Pt(diolefin)Cl(PR_3)]$^+$ are much less susceptible to nucleophilic attack than those in the chlorine-bridged complexes. The platinum complexes were recovered unchanged from refluxing methanol, but addition of methanol to [Pd(cod)Cl(PPh_3)][BF_4] resulted in formation of [$PdCl_2(PPh_3)_2$]. Reaction of silver(I) acetate with [Pt(cod)Cl(PMe_2Ph)][BF_4] resulted in replacement of the chloride ligand by acetate rather than nucleophilic attack on the diolefin. It is probable that the presence of phosphine in the co-ordination sphere of the metal reduces the degree of polarisation of the co-ordinated olefins.

EXPERIMENTAL

The techniques and spectroscopic methods were as previously described;[1] conductivities were determined for *ca.* 10^{-3} mol dm^{-3} solutions in nitromethane.

[M(diolefin)Cl_2] [M = Pd *or* Pt; *diolefin* = *cyclo-octa-*1,5-*diene*(*cod*), *norborna-*2,5-*diene*(*nbd*), *or* endo-*dicyclopentadiene*(*dcpd*)].—Published methods were used for M = Pd.[5,9]

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Dichloro(η-*cyclo-octa*-1,5-*diene*)*platinum*(II).—A mixture of $[PtCl_2(SEt_2)_2]$ (2.1 g) and cod (10 cm^3) was heated under reflux for 2 h, after which the colourless crystals formed were filtered off, washed with hexane, and dried *in vacuo* to give the product (1.51 g, 89%), m.p. 220—250 °C (lit.,[4] 220—278 °C) (Found: C, 25.8; H, 3.2. Calc. for $C_8H_{12}Cl_2Pt$: C, 25.7; H, 3.2%). A similar procedure with nbd and 4 h reflux gave *dichloro*(η-*norborna*-2,5-*diene*)*platinum*(II) (60%), m.p. 200—250 °C (lit.,[10] 230—280 °C) (Found: C, 23.7; H, 2.3. Calc. for $C_7H_8Cl_2Pt$: C, 23.5; H, 2.3%), and with dcpd and 2.5 h reflux followed by purification with charcoal gave *dichloro*(η-endo-*dicyclopentadiene*)*platinum*(II) (40%), m.p. 200—220 °C (lit.,[4] 200—220 °C) (Found: C, 30.4; H, 3.1. Calc. for $C_{10}H_{12}Cl_2Pt$: C, 30.2; H, 3.0%).

Di-μ-*chloro-bis*[(η-*cyclo-octa*-1,5-*diene*)*palladium*(II)] *Tetrafluoroborate*.—Addition of $[Et_3O][BF_4]$ (0.4 g, 2.1 mmol) in dichloromethane (6 cm^3) to a refluxing solution of $[Pd(cod)Cl_2]$ (0.51 g, 1.75 mmol) gave a dark yellow solution during 15 min. On cooling in ice, yellow needles were precipitated. These were washed with dichloromethane to give the *product* (0.44 g, 75%), m.p. 128—132 °C (decomp.) (Found: C, 28.6; H, 3.6; Cl, 10.5. $C_{16}H_{24}B_2Cl_2F_8Pd_2$ requires C, 28.5; H, 3.6; Cl, 10.5%); $\nu_{asym}(BF_4)$ at 1 050vs,br cm^{-1}, ν(PdCl) at 330 and 295 cm^{-1} (Nujol); Λ_M 150 S cm^2 mol^{-1}. Similarly obtained were: *di*-μ-*chloro-bis*[(η-*norborna*-2,5-*diene*)*palladium*(II)] *tetrafluoroborate* (30 min reflux) as a yellow-green powder too unstable for analysis, $\nu_{asym}(BF_4)$ at 1 050vs,br cm^{-1}, ν(PdCl) at 332 and 272 cm^{-1} (Nujol), Λ_M 130 S cm^2 mol^{-1}; *di*-μ-*chloro-bis*[(η-*cyclo-octa*-1,5-*diene*)*platinum*(II)] *tetrafluoroborate* (45 min reflux) precipitated from hexane and recrystallised from acetone–hexane as a colourless *product* (60%), m.p. 125—130 °C (Found: C, 22.4; H, 3.1; Cl, 7.8. $C_{10}H_{24}B_2Cl_2F_8Pt_2$ requires C, 22.6; H, 2.8; Cl, 8.2%), $\nu_{asym}(BF_4)$ at 1 050vs,br cm^{-1}, ν(PtCl) at 340 and 320 cm^{-1} (Nujol), Λ_M 165 S cm^2 mol^{-1}; and *di*-μ-*chloro-bis*[(η-*norborna*-2,5-*diene*)*platinum*(II)] *tetrafluoroborate* (1 h reflux) from acetone–hexane as an off-white *powder* (45%), m.p. 110—115 °C (decomp.) (Found: C, 19.9; H, 2.3. $C_{14}H_{16}B_2Cl_2F_8Pt_2$ requires C, 20.5; H, 2.0%), $\nu_{asym}(BF_4)$ at 1 050vs,br cm^{-1}, ν(PtCl) at 310 and 265 cm^{-1} (Nujol), Λ_M 145 S cm^2 mol^{-1}.

Reactions of $[Pd_2(cod)_2Cl_2][BF_4]_2$.—(a) *With methanol*. Addition of methanol (1 cm^3) to dark yellow $[Pd_2(cod)_2Cl_2][BF_4]_2$ immediately gave a pale yellow solid, *di*-μ-*chloro-bis*[5,6-η-2-*methoxycyclo-oct*-5-*enyl*)*palladium*(II)], m.p. 125—135 °C (lit.,[4] 130—135 °C) (0.13 g, 92%), identified by comparison (i.r.) with an authentic sample.

(b) *With acetic acid*. Addition of the complex (0.2 g) to refluxing glacial acetic acid (5 cm^3) gave a pale yellow solution during 3 h, which was evaporated to a pale yellow residue. This was washed with chloroform and hexane to give *di*-μ-*chloro-bis*[(5,6-η-2-*acetoxycyclo-oct*-5-*enyl*)*palladium*(II)] (0.16 g, 90%), m.p. 90—110 °C (lit.,[11] 95—120 °C), identified by comparison (i.r., ^{1}H n.m.r.) with an authentic sample.

(c) *With water*. Deoxygenated water (0.01 cm^3) was added to a solution of the complex (0.1 g) in acetone (10 cm^3). The yellow colour was immediately discharged and an off-white solid precipitated. Rapid recrystallisation from chloroform–hexane gave *di*-μ-*chloro-bis*[(5,6-η-2-*hydroxycyclo-oct*-5-*enyl*)*palladium*(II)] as a white solid (0.053 g, 66%), m.p. 113—116 °C (Found: C, 36.4; H, 4.8; Cl, 14.2. $C_{16}H_{26}Cl_2O_2Pd_2$ requires C, 36.0; H, 4.9; Cl, 13.3%).

(d) *With triphenylphosphine*. Triphenylphosphine (0.039 g, 0.15 mmol) in acetone (15 cm^3) was added slowly to a stirred solution of the complex (0.05 g, 0.074 mmol) in acetone (10 cm^3). A bright yellow solid (m.p. 245—250 °C) separated and was shown to be di-μ-chloro-bis[bis(triphenylphosphine)palladium(II)] tetrafluoroborate (0.055 g, 50%) by comparison (i.r.) with an authentic sample,[1] and the filtrate contained unchanged starting complex. A similar result was obtained when the reagents were mixed at −78 °C and the solution allowed to warm slowly to room temperature.

Reaction of $[Pt_2(cod)_2Cl_2][BF_4]_2$ *with Triphenylphosphine*.—Triphenylphosphine (0.093 g, 0.36 mmol) in acetone (10 cm^3) was added slowly to a stirred solution of the complex (0.15 g, 0.18 mmol) in acetone (25 cm^3). The colourless crystals that separated immediately were washed with acetone and with hexane, and dried to give *chloro*(η-*cyclo-octa*-1,5-*diene*)(*triphenylphosphine*)*platinum*(II) *tetrafluoroborate* (0.19 g, 81%), m.p. 155—160 °C (Found: C, 45.6; H, 3.6; Cl, 5.5. $C_{26}H_{27}BClF_4PPt$ requires C, 45.4; H, 3.9; Cl, 5.2%).

Preparation of Complexes $[M(diolefin)Cl(PR_3)]Y$.—The starting materials *sym,trans*-$[M_2Cl_4(PR_3)_2]$ were prepared by an established procedure[12] and were characterised by m.p., i.r. spectra, and elemental analyses. The preparative methods and characterisation of the new complexes are summarised in the Table.

Chloro(η-*cyclo-octa*-1,5-*diene*)(*dimethylphenylphosphine*)-*platinum*(II) *Tetrafluoroborate*.—Cyclo-octa-1,5-diene (2 cm^3) was added to a solution of $[Pt_2Cl_4(PMe_2Ph)_2]$ (0.13 g, 0.16 mmol) and $[Et_3O][BF_4]$ (0.075 g, 0.39 mmol) in dichloromethane (15 cm^3) and the solution became colourless during 10 min. Evaporation to half-volume followed by addition of hexane (5 cm^3) gave the *product* as colourless crystals (0.17 g, 92%).

Other complexes of this type were prepared in a similar manner with $SFO_2(OMe)–C_6H_6$ or $Na[ClO_4]–Me_2CO$ in place of $[Et_3O][BF_4]$ as appropriate. The reactions were complete within 30 min and yields were 80—90% for cod and nbd complexes. Complexes of PPh_3 separated directly; with others addition of hexane was necessary. Recrystallisation was from dichloromethane–hexane. The complex of dcpd was obtained pure only after treatment with charcoal (yield 25%). Attempts to prepare complexes of dcpd containing PPh_3 or PBu_3 led to intractable brown oils.

Reaction of Chloro(η-*cyclo-octa*-1,5-*diene*)(*dimethylphenylphosphine*)*platinum*(II) *Tetrafluoroborate with Silver*(I) *Acetate*.—Silver(I) acetate (0.017 g, 0.1 mmol) in acetone (20 cm^3) was added to a stirred solution of the complex (0.056 g, 0.1 mmol) in chloroform (10 cm^3). After 15 min, AgCl was removed by filtration, and addition of hexane to the filtrate precipitated a colourless solid which was recrystallised from chloroform–hexane to give *acetato*(η-*cyclo-octa*-1,5-*diene*)(*dimethylphenylphosphine*)*platinum*(II) *tetrafluoroborate* as colourless needles (0.043 g, 73%), m.p. 110—112 °C (Found: C, 36.5; H, 4.1. $C_{18}H_{26}BF_4O_2PPt$ requires C, 36.8; H, 4.3%), ν(C=O) at 1 630 cm^{-1}, ν(C–O) at 1 295 cm^{-1}, $\nu_{asym}(BF_4)$ at 1 050vs,br cm^{-1}.

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Reaction of Chloro(η-cyclo-octa-1,5-diene)(triphenylphosphine)palladium(II) Tetrafluoroborate with Methanol.—Methanol (2 cm^3) was added to the solid complex (0.22 g). From the resulting red solution, *trans*-dichlorobis(triphenylphosphine)palladium(II) (0.9 g, 87%) was precipitated, and was identified by comparison (m.p., i.r.) with an authentic sample. Evaporation of the supernatant gave an intractable red oil.

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