

Cationic Palladium and Platinum Complexes with Diolefin Ligands †

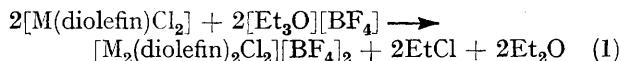
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Chlorine-bridged complexes $[M_2(\text{diolefin})_2Cl_2][BF_4]_2$ have been prepared from $[M(\text{diolefin})Cl_2]$ [$M = Pd$ or Pt ; diolefin = cyclo-octa-1,5-diene (cod) or norborna-2,5-diene (nbd)] and $[Et_3O][BF_4]$. The complex $[Pd(\text{cod})_2Cl_2][BF_4]_2$ 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 $[Pt(\text{cod})Cl(PPh_3)][BF_4]$. Complexes $[M(\text{diolefin})Cl(PR_3)]X$ ($X = SFO_3, BF_4,$ 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 $[M(\text{diolefin})Cl_2]$ [$M = Pd$ or Pt ; diolefin = cyclo-octa-1,5-diene (cod) or norborna-2,5-diene (nbd)]



proceed in a similar manner [equation (1)]. The complexes $[M_2(\text{diolefin})_2Cl_2][BF_4]_2$ ($M = Pd$ 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 $\nu(M-Cl)$ 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 $[Pd_2(\text{nbd})_2Cl_2][BF_4]_2$ decomposes within a few minutes in air and a satisfactory analysis was not obtained; $[Pd_2(\text{cod})_2Cl_2][BF_4]_2$ 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 $[Pd(\text{pd})(C_{10}H_{12}OMe)]$ (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 $[M(\text{dcpd})Cl_2]$ are very susceptible to nucleophilic attack,⁵ the failure to obtain the much more reactive cationic complex is readily understood.

* M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, 1973, **12**, 991.

³ P. M. Druce, M. F. Lappert, and P. N. K. Riley, *J.C.S. Dalton*, 1972, 438.

⁴ B. F. G. Johnson, J. Lewis, and D. A. White, *J. Chem. Soc. (A)*, 1970, 1738.

⁵ J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2496, 3413.

† No reprints available.

¹ C. Eaborn, N. Farrell, J. L. Murphy, and A. Pidcock, *J. Organometallic Chem.*, 1973, **55**, C68; *J.C.S. Dalton*, 1976, 58; P. M. Treichel, K. P. Wagner, and W. J. Knebel, *Inorg. Chim. Acta*, 1972, **6**, 674.

As expected, the susceptibility of the co-ordinated diolefins to nucleophilic attack was much greater in the cationic complexes than in $[M(\text{diolefin})\text{Cl}_2]$. Whereas the uncharged complexes react only with the conjugate bases of alcohols or carboxylic acids (*e.g.*, $\text{MeOH}-\text{Na}_2[\text{CO}_3]$ ⁵ or $\text{Ag}[\text{O}_2\text{CMe}]$ ⁶), the complex $[\text{Pd}_2(\text{cod})_2\text{Cl}_2]-[\text{BF}_4]_2$ reacted very rapidly with MeOH , MeCO_2H , or H_2O to form $[\text{Pd}_2(2\text{-Rcot})_2\text{Cl}_2]$ ($\text{R} = \text{MeO}$, MeCO_2 , or HO). The 2-hydroxycyclo-oct-5-enyl complex ($\text{R} = \text{HO}$) is air stable, soluble in benzene and chlorinated solvents, and is a non-conductor in nitromethane. The i.r. spectrum had $\nu(\text{OH})$ at $3\ 800-3\ 500\ \text{cm}^{-1}$ and there was no absorption indicative of $[\text{BF}_4]^-$. The ^1H n.m.r. spectrum of a CDCl_3 solution had a multiplet at $\tau\ 4.25$ ($I = 2$) from the olefinic protons, a complex region

which chloride is removed by reaction with the alkylating agent, is analogous to the procedure adopted by Church and Mays⁸ for promoting the displacement of chloride ligands by neutral donors. These workers carried out reactions in acetone in the presence of $\text{Na}[\text{ClO}_4]$, which led to the precipitation of chloride as NaCl and the formation of perchlorate salts. We obtained $[\text{Pt}(\text{cod})\text{Cl}(\text{PBU}_3)][\text{ClO}_4]$ by this method (Table). Some complexes of the type $[\text{Pt}(\text{cod})\text{Cl}(\text{PR}_3)][\text{BF}_4]$ have been obtained previously by treatment of $[\text{Pt}(2\text{-Rcot})\text{Cl}(\text{PR}_3)]$ [$\text{R} = \text{CH}(\text{COMe})_2$] with $[\text{Ph}_3\text{C}][\text{BF}_4]$;⁴ the method of equation (2) is clearly more convenient. The complexes $[\text{MCl}(\text{PR}_3)(\text{diolefin})]\text{X}$ are generally insoluble in organic solvents, and satisfactory n.m.r. spectra were obtained only for the more soluble complexes.

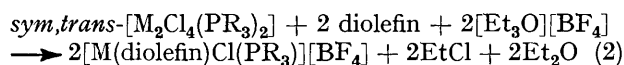
Characterisation of complexes $[\text{Pt}(\text{diolefin})\text{Cl}(\text{PR}_3)]\text{X}$

Diolefin	M	PR_3	X	M.p. ($\theta_c/^\circ\text{C}$)	Analysis (%)				Λ_{M}^a $\text{S cm}^2\ \text{mol}^{-1}$	$\bar{\nu}(\text{M}-\text{Cl})$ cm^{-1}	τ	^1H N.m.r. (olefinic protons) ^b			
					Found		Calc.					<i>trans</i> to P		<i>trans</i> to Cl	
					C	H	C	H				$^3J(\text{PPtCH})$ Hz	$^2J(\text{PtCH})$ Hz	τ	$^2J(\text{PtCH})$ 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%).

$\tau\ 6.5-7.0$ ($I = 2$) from the protons on carbon substituted by Pd or OH, resonances from methylene groups $\tau\ 7.0-8.0$ ($I = 8$), and a singlet at $\tau\ 8.5$ ($I = 1$), assigned to the hydroxyl proton, which disappeared on addition of D_2O . The spectrum is similar to that reported for $[\text{Pd}_2\text{Br}_2(2\text{-HOcot})_2]$.⁷

A reaction between $[\text{Pt}(\text{cod})_2\text{Cl}_2][\text{BF}_4]_2$ (1 mol) and PPh_3 (2 mol) in acetone formed the cationic diolefin complex $[\text{Pt}(\text{cod})\text{Cl}(\text{PPh}_3)][\text{BF}_4]$ in high yield. However, reaction of the corresponding palladium complex resulted in displacement of the diolefin ligand and formation of $[\text{Pd}_2\text{Cl}_2(\text{PPh}_3)_4][\text{BF}_4]_2$ in *ca.* 50% yield. Because the cationic complexes $[\text{M}(\text{diolefin})\text{Cl}(\text{PR}_3)]-[\text{BF}_4]$ were not available by this route for $\text{M} = \text{Pd}$, we employed an alternative synthesis [equation (2)] which avoids the use of free phosphines. The complexes prepared by this route or by use of $\text{SFO}_2(\text{OMe})$ in place



of $[\text{Et}_3\text{O}][\text{BF}_4]$ are given in the Table. This method, in

The olefinic bonds in the complexes $[\text{Pt}(\text{diolefin})\text{Cl}(\text{PR}_3)]^+$ 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 $[\text{Pd}(\text{cod})\text{Cl}(\text{PPh}_3)][\text{BF}_4]$ resulted in formation of $[\text{PdCl}_2(\text{PPh}_3)_2]$. Reaction of silver(I) acetate with $[\text{Pt}(\text{cod})\text{Cl}(\text{PMe}_2\text{Ph})][\text{BF}_4]$ 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.

$[\text{M}(\text{diolefin})\text{Cl}_2]$ [$\text{M} = \text{Pd}$ or Pt ; *diolefin* = *cyclo-octa-1,5-diene* (cod), *norborna-2,5-diene* (nbd), or *endo-dicyclopentadiene* (dcpd)].—Published methods were used for $\text{M} = \text{Pd}$.^{5,9}

⁶ C. B. Anderson and B. J. Burreson, *J. Organometallic Chem.*, 1967, **7**, 181.

⁷ D. A. White, *J. Chem. Soc. (A)*, 1971, 145.

⁸ M. J. Church and M. J. Mays, *J. Chem. Soc. (A)*, 1968, 3074.

⁹ R. A. Alexander, N. C. Baenziger, C. Carpenter, and J. A. Doyle, *J. Amer. Chem. Soc.*, 1960, **82**, 535.

Dichloro(η-cyclo-octa-1,5-diene)platinum(II).—A mixture of $[\text{PtCl}_2(\text{SEt}_2)_2]$ (2.1 g) and cod (10 cm³) 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 C₈H₁₂Cl₂Pt: 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 C₇H₈Cl₂Pt: 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 C₁₀H₁₂Cl₂Pt: C, 30.2; H, 3.0%).

Di-μ-chloro-bis[(η-cyclo-octa-1,5-diene)palladium(II)] tetrafluoroborate.—Addition of $[\text{Et}_3\text{O}][\text{BF}_4]$ (0.4 g, 2.1 mmol) in dichloromethane (6 cm³) to a refluxing solution of $[\text{Pd}(\text{cod})\text{Cl}_2]$ (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. C₁₆H₂₄B₂Cl₂F₈Pd₂ requires C, 28.5; H, 3.6; Cl, 10.5%); $\nu_{\text{asym}}(\text{BF}_4)$ at 1 050vs,br cm⁻¹, $\nu(\text{PdCl})$ at 330 and 295 cm⁻¹ (Nujol); Λ_{M} 150 S cm² 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, $\nu_{\text{asym}}(\text{BF}_4)$ at 1 050vs,br cm⁻¹, $\nu(\text{PdCl})$ at 332 and 272 cm⁻¹ (Nujol), Λ_{M} 130 S cm² 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. C₁₀H₂₄B₂Cl₂F₈Pt₂ requires C, 22.6; H, 2.8; Cl, 8.2%); $\nu_{\text{asym}}(\text{BF}_4)$ at 1 050vs,br cm⁻¹, $\nu(\text{PtCl})$ at 340 and 320 cm⁻¹ (Nujol), Λ_{M} 165 S cm² 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. C₁₄H₁₆B₂Cl₂F₈Pt₂ requires C, 20.5; H, 2.0%); $\nu_{\text{asym}}(\text{BF}_4)$ at 1 050vs,br cm⁻¹, $\nu(\text{PtCl})$ at 310 and 265 cm⁻¹ (Nujol), Λ_{M} 145 S cm² mol⁻¹.

Reactions of $[\text{Pd}_2(\text{cod})_2\text{Cl}_2][\text{BF}_4]_2$.—(a) *With methanol*. Addition of methanol (1 cm³) to dark yellow $[\text{Pd}_2(\text{cod})_2\text{Cl}_2][\text{BF}_4]_2$ 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 cm³) 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., ¹H n.m.r.) with an authentic sample.

(c) *With water*. Deoxygenated water (0.01 cm³) was added to a solution of the complex (0.1 g) in acetone (10 cm³). 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. C₁₆H₂₆Cl₂O₂Pd₂ requires C, 36.0; H, 4.9; Cl, 13.3%).

(d) *With triphenylphosphine*. Triphenylphosphine (0.039 g, 0.15 mmol) in acetone (15 cm³) was added slowly to a stirred solution of the complex (0.05 g, 0.074 mmol) in acetone (10 cm³). 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 $[\text{Pt}_2(\text{cod})_2\text{Cl}_2][\text{BF}_4]_2$ with Triphenylphosphine.—Triphenylphosphine (0.093 g, 0.36 mmol) in acetone (10 cm³) was added slowly to a stirred solution of the complex (0.15 g, 0.18 mmol) in acetone (25 cm³). 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. C₂₆H₂₇BClF₄PPh₃ requires C, 45.4; H, 3.9; Cl, 5.2%).

Preparation of Complexes $[\text{M}(\text{diolefin})\text{Cl}(\text{PR}_3)]\text{Y}$.—The starting materials *sym,trans*- $[\text{M}_2\text{Cl}_4(\text{PR}_3)_2]$ were prepared by an established procedure¹² 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 cm³) was added to a solution of $[\text{Pt}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_2]$ (0.13 g, 0.16 mmol) and $[\text{Et}_3\text{O}][\text{BF}_4]$ (0.075 g, 0.39 mmol) in dichloromethane (15 cm³) and the solution became colourless during 10 min. Evaporation to half-volume followed by addition of hexane (5 cm³) gave the product as colourless crystals (0.17 g, 92%).

Other complexes of this type were prepared in a similar manner with SFO₂(OMe)–C₆H₆ or Na[ClO₄]–Me₂CO in place of $[\text{Et}_3\text{O}][\text{BF}_4]$ as appropriate. The reactions were complete within 30 min and yields were 80–90% for cod and nbd complexes. Complexes of PPh₃ 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 PPh₃ or PBu₃ 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 cm³) was added to a stirred solution of the complex (0.056 g, 0.1 mmol) in chloroform (10 cm³). 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. C₁₈H₂₆BF₄O₂PPh₂ requires C, 36.8; H, 4.3%); $\nu(\text{C}=\text{O})$ at 1 630 cm⁻¹, $\nu(\text{C}-\text{O})$ at 1 295 cm⁻¹, $\nu_{\text{asym}}(\text{BF}_4)$ at 1 050vs,br cm⁻¹.

¹⁰ E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3178.

¹¹ C. B. Anderson and B. J. Burreson, *J. Organometallic Chem.*, 1967, 7, 181.

¹² A. C. Smithies, M. Rycheck, and M. Orchin, *J. Organometallic Chem.*, 1968, 12, 199.

Reaction of Chloro(η -cyclo-octa-1,5-diene)(triphenylphosphine)palladium(II) Tetrafluoroborate with Methanol.—Methanol (2 cm³) 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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