Preparation of Platinum π-Olefin Complexes from Bis(1,5-diphenylpenta-1,4-dien-3-one)platinum(0)

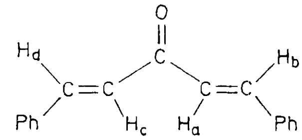
By **Walter J. Cherwinski, Brian F. G. Johnson,** and **Jack Lewis,*** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

Zerovalent platinum olefin and acetylene complexes $Pt(OL)L_2$ have been isolated for OL = C_2Cl_4, C_2F_4, $CF_3C{\equiv}CCF_3$, $(CF_3)_2CO$, and CS_2 (but not for non-activated olefins) for a variety of phosphine and arsine ligands L from a reaction with the air-stable derivative bis(1,5-diphenylpenta-1,4-dien-3-one), $Pt(dpo)_2$. An intermediate complex, $Pt(dpo)L_2$, involving metal co-ordination to one double bond of the diene ligand, undergoes olefin displacement by OL to give the same derivatives. ^1H and ^{13}C N.m.r. spectra for the products $Pt(dpo)L_2$ and ^{19}F n.m.r. spectra for the species $Pt(OL)(PEt_3)_2$ where OL = C_2F_4 and $CF_3C{\equiv}CCF_3$ are reported.

MANY zerovalent-metal olefin and acetylene complexes[1] of the type $M(OL)L_2$ (M = Ni, Pd, or Pt; L = tertiary phosphine) have been synthesised and examined. Typically, for platinum such derivatives have been most common for L = PPh_3, presumably because of the ease of their formation and the nucleophilic reactivity[2] of $Pt(PPh_3)_n$ (n = 2, 3, or 4) towards numerous unsaturated substrates. Only recently have similar species ML_4[3] been isolated for a wider range of stabilizing ligands L, including PEt_3, $P(OEt)_3$, PMe_2Ph, and $PMePh_2$.

However, the relatively few examples of metal–olefin complexes stabilized by more basic phosphine ligands PR_3, where R = alkyl, are limited to highly activated olefins and acetylenes such as in platinum complexes[4,5] of tetracyanoethylene for R = Me and Et and dicyanoacetylene for R = Et. A hexafluoropropene complex of zerovalent nickel[6] has been prepared for R = Et by displacement of cyclo-octa-1,5-diene from $Ni(C_3F_6)(cod)$. Similarly, the possible application of ligand displacement as a route to zerovalent platinum derivatives prompted us to investigate[7] reactions of the recently reported

(dpo)



air-stable complex[8] bis(1,5-diphenylpenta-1,4-dien-3-one)platinum(0), $Pt(dpo)_2$.

---

[1] *E.g.* see R. Ugo, *Co-ordination Chem. Rev.*, 1968, **3**, 319 and references therein.

[2] F. R. Hartley, *Chem. Rev.*, 1967, **69**, 799.

[3] H. C. Clark and K. Itoh, *Inorg. Chem.*, 1971, **8**, 1707.

[4] H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 1971, 416.

[5] G. L. McClure and W. H. Baddley, *J. Organometallic Chem.*, 1970, **25**, 261.

[6] C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 1647.

[7] W. J. Cherwinski, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1973, **52**, C61.

[8] P. M. Maitlis and K. Moseley, *Chem. Comm.*, 1971, 982.

In the absence of olefins, treatment of a toluene solution of Pt(dpo)$_2$ with an excess of L results in a gradual colour change from purple to orange. From the resulting solutions, air-stable, yellow-orange products of stoicheiometry Pt(dpo)L$_2$, (I), can be isolated for L = PPh$_3$, PPh$_2$Me, PEt$_3$, AsPh$_3$, and AsEt$_3$ [Scheme, reaction (*i*), *n* = 2—10]. Pt(dpo)(PPh$_3$)$_2$ could also be formed by reaction of Pt(PPh$_3$)$_4$ with an excess of 1,5-diphenylpenta-1,4-dien-3-one.

These derivatives were identified by their i.r. and n.m.r. spectra and elemental analyses (Table 1). Ishii and co-workers[9] have described similar behaviour for Pd(dpo)$_2$ with *N*-donor ligands, although, in a reaction analogous to (*i*), Pd(PPh$_3$)$_4$ is the major product. For platinum(0), PtL$_4$ can be isolated from sequence (*i*) only for the strongly π-acidic ligand L = AsPh$_3$ when $n \geqslant 4$, while for $n = 2$ this reaction gives a high yield of (I). The ^{1}H n.m.r. spectrum of Pt(dpo)(PPh$_3$)$_2$ in CDCl$_3$: (C$_6$H$_5$, H$_a$), τ 2·8 (41H); (H$_b$), τ 4·01 (1H), doublet with J(H$_a$H$_b$) 16·5 Hz; (H$_c$, H$_d$), τ 5·87 (2H), multiplet with ^2J(PtH) 55 Hz; and its similarity to the spectra of the products of reaction (*iii*) with 4-phenylbut-3-en-2-one and 1,3-diphenylprop-2-en-1-one supports a structure in which the metal is bound by one double bond of 1,5-diphenylpenta-1,4-dien-3-one, while the other remains free.

TABLE 1

Physical properties of Pt(dpo)L$_2$ and derivatives

		Analysis (%)			
		Calc.		Found	
Compound	M.p./°C	C	H	C	H
Pt(dpo)(PPh$_3$)$_2$	188—190	66·73	4·65	66·35	4·8
Pt(dpo)(AsPh$_3$)$_2$	161—163	61·10	4·26	60·6	4·3
Pt(dpo)(PEt$_3$)$_2$		52·32	6·66	52·1	6·45
Pt(dpo)(AsEt$_3$)$_2$	Oil	46·34	5·86	46·35	5·8
Pt(ba)(PPh$_3$)$_2$	181—184	63·81	4·66	64·2	4·7
Pt(bap)(PPh$_3$)$_2$	184—187	66·01	4·56	66·15	4·7
Pt(C$_2$Cl$_4$)(AsPh$_3$)$_2$ [a]		42·02	2·82	42·6	2·8
Pt(C$_2$F$_4$)(PEt$_3$)$_2$	Oil	31·70	5·66	31·6	5·6 [b]
Pt(CF$_3$C≡CCF$_3$)(PEt$_3$)$_2$ [c]	74—76	32·38	5·10	32·95	4·8 [d]

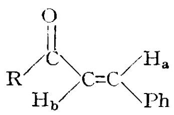
[a] Isolated as dichloromethane solvate Pt(C$_2$Cl$_4$)(AsPh$_3$), 2CH$_2$Cl$_2$. [b] Fluorine analysis: 1·3; calc. 1·41%. [c] Purified by sublimation at 80°. [d] Fluorine analysis: 1·8; calc. 1·92%.

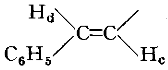
By analogy with the n.m.r. spectra for the derivatives[10] M(OL)(PPh$_3$)$_2$ where OL = cinnamaldehyde and ethyl *trans*-cinnamate (Table 2) the complex resonance at τ 5·87 p.p.m. can be assigned to the protons of the co-ordinated olefin while the two proton resonances of the free double bond occur at τ 4·01 and τ *ca.* 2·80 p.p.m. (obscured by C$_6$H$_5$ absorptions). The shift to higher field of the olefinic proton signals compared to the free values is typical upon co-ordination to low-valent transition metals.[11]

The co-ordinated olefinic ends are also observed in ^{13}C n.m.r. spectra of Pt(dpo)(PEt$_3$)$_2$ and Pt(dpo)(AsEt$_3$)$_2$ (Table 3) where both the chemical shifts and the magnitude of metal–carbon coupling are typical for platinum π-olefin derivatives.[12]

TABLE 2

^{1}H N.m.r. data for complexes Pt(OL)L$_2$ in CDCl$_3$ solution where OL =

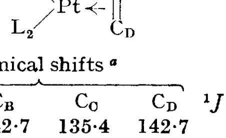


		Not co-ordinated (p.p.m.)		Co-ordinated (p.p.m.) [a]	
R	L	τ(H$_a$)	τ(H$_b$)	τ(H$_c$,H$_d$)	^2J(PtCH) /Hz
	Free	2·26	2·94 [b]		
	PPh$_3$	*c*	4·01	5·87	*ca.* 55
	AsPh$_3$	*c*	3·65	5·61	66
	PPh$_2$Me	*c*	3·46	6·51	*d*
	PEt$_3$	*c*	3·21	6·25	*d*
	PEt$_3$ [e]	*c*	4·12	5·59	*d*
	AsEt$_3$	*c*	3·18	6·19	*ca.* 55
C$_6$H$_5$	Free	2·29	2·8		
	PPh$_3$			*ca.* 5·6	*d*
CH$_3$ [f]	Free	*ca.* 2·7	3·41		
	PPh$_3$			6·14	*ca.* 60
EtO [g]	Free	2·22	3·52		
	PPh$_3$			*ca.* 6·3	*d*
H [g]	Free	2·94	3·45		
	PPh$_3$			6·24	*ca.* 60

[a] Co-ordinated olefin resonances observed as complicated multiplets. [b] For all complexes where R = C$_6$H$_5$C$_2$H$_2$, ^3J(H$_a$H$_b$) 16·5 Hz. [c] Resonance obscured by phenyl group absorptions. [d] Not assignable. ^3J(PH) for co-ordinated olefin hydrogens not assignable. [e] Evidence for a related derivative; see Experimental section. [f] τ(CH$_3$) = 7·79 (free), 8·52 (complex). [g] Ref. 10.

TABLE 3

^{13}C N.m.r. data for complexes Pt(dpo)L$_2$



	Chemical shifts [a]					
L$_{1,2}$	C$_A$	C$_B$	C$_C$	C$_D$	^1J(PtC$_C$) [b]	^1J(PtC$_D$)
Free dpo	135·4	142·7	135·4	142·7		
PEt$_3$	124·6	134·8	49·7	61·0	235 [c]	180 [c]
AsEt$_3$	123·0	135·8	46·3	58·0	275	185

[a] Chemical shifts in p.p.m. from tetramethylsilane. Spectra run in CDCl$_3$ solution. Assignations made by use of lanthanoid shift reagent studies in conjunction with selective irradiation and decoupling of proton signals (B. Birdsall, J. Feeney, J. A. Glasel, R. J. P. Williams, and A. V. Xavier, *Chem. Comm.*, 1971, 1473). [b] Coupling constants in Hz. [c] ^2J(P$_1$–C$_C$) = 0, ^2J(P$_2$–C$_C$) = 37, ^2J(P$_1$–C$_D$) = ^2J(P$_2$–C$_D$) = 5.

This mode of bonding contrasts to the proposed situation[8] in Pt(dpo)$_2$ where ' sideways ' co-ordination is thought to occur through both carbonyl groups. For

---

[9] T. Ito, Y. Takahashi, and Y. Ishii, *J.C.S. Chem. Comm.*, 1972, 629.

[10] S. Cenini, R. Ugo, and G. La Monica, *J. Chem. Soc.* (*A*), 1971, 409.

[11] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 1.

[12] W. J. Cherwinski, B. F. G. Johnson, J. Lewis, and J. Norton, in the press.

this latter complex, we have observed no co-ordinated double bond in the ^{13}C n.m.r. spectrum.

The carbon–carbon double bond i.r. stretching frequency for co-ordinated olefin could not be assigned,[10] owing to a shift into the complex region below 1480 cm^{-1}; ν(C=C) = 1621vs and 1624vs cm^{-1} for free dpo and $Pt(dpo)_2$ respectively.

Reactions of the complex $Pt(dpo)(PPh_3)_2$ with activated olefins or acetylenes proceed quantitatively, with displacement of dba, affording the known derivatives $Pt(OL)(PPh_3)_2$ where OL = C_2Cl_4, $CF_3C{\equiv}CCF_3$, $(CF_3)_2CO$, or CS_2 [sequence (*ii*)]. Alternatively, these products may be isolated directly from the reaction of $Pt(dpo)_2$ with an excess of olefin in the presence of L [sequence (*iv*)]. Ishii and co-workers[9,13] have isolated related olefin derivatives of palladium by a similar procedure.

Although similar reactions occur for L = $AsPh_3$ and OL = C_2Cl_4 and for L = PPh_2Me and OL = $(CF_3)_2CO$ or C_2Cl_4, in no instance does ethylene displace co-ordinated dpo. Indeed, exchange of C_2H_4 in $Ni(C_2H_4)(PPh_3)_2$ with more activated olefins is a common route[14] to similar derivatives $Ni(OL)(PPh_3)_2$.

The favoured product in such displacement reactions may be accounted for by the presence of electron-withdrawing substituents on the olefin. Activity orders in displacement reactions have been reported[15,16] for series of olefins and acetylenes, while the stability of tetrachloroethylene derivatives (hence the high activity of C_2Cl_4) has been confirmed in the formation of $Pt(C_2Cl_4)(PPh_3)_2$ from displacement of OL = stilbene and diphenylacetylene from $Pt(OL)(PPh_3)_2$. By this criterion, the ease of displacement here of dpo by OL suggests a position low in any such series.

When L = PEt_3 and OL = $CF_3C{\equiv}CCF_3$, reaction (*i*) for $Pt(dpo)(PEt_3)_2$ proceeds quantitatively to yield white, crystalline $Pt(CF_3C{\equiv}CCF_3)(PEt_3)_2$ identified by elemental analysis, i.r. and n.m.r. spectra (^1H and ^{19}F). The corresponding complexes $Pt(OL)(PEt_3)_2$ are isolated in lower yield where OL = C_2Cl_4 or C_2F_4. For this latter derivative, the ^{19}F n.m.r. spectrum is qualitatively similar to that reported[17] for the analogue where L = PPh_3, while the low value of $^2J(PtF)$ 280 Hz[18] may indicate a relatively weak platinum–olefin bond.

There is evidence that the white crystalline compounds which are recovered in high yield for L = PEt_3 and OL = $(CF_3)_2CO$ or $(CF_3)_2CNH$ are products of cyclization of OL with co-ordinated dpo although the exact nature of such species could not be determined (see Experimental section). These observations are consistent with the enhancement of nucleophilicity in the platinum system by the strong σ-donor ligand PEt_3 and the known[19] cyclization reactions of the ligands OL in related systems.

In view of the recent studies[9] on $Pd(dpo)_2$, our results suggest that further zerovalent platinum derivatives may be synthesised for a greater variety of ligands, L, and olefins or acetylenes, OL.

EXPERIMENTAL

I.r. spectra were recorded on solutions in chloroform on a Perkin-Elmer 257 or 457 instrument. ^1H N.m.r. spectra were obtained on a Varian HA100 instrument while ^{19}F and ^{13}C spectra were recorded on a Varian XL 100 spectrometer. Microanalyses were performed at the Chemical Laboratory, Cambridge.

All olefinic and phosphine ligands were purified (by distillation or recrystallization) before use. Reactions were carried out in dried solvents in sealed evacuated Carius tubes although the work-up of most reaction mixtures was done in air.

The identities of known derivatives were confirmed by comparison of their properties with those reported in the literature. Analytical data, physical properties, and spectroscopic parameters for the new compounds obtained are summarized in Tables 1—3. Reaction pathways are outlined in the Scheme.

Preparation of Bis(1,5-*diphenylpenta*-1,4-*dien*-3-*one*)*platinum*.—$Pt(dpo)_2$ was prepared by the method of Maitlis and Moseley[8] with some modification.

A solution of 1,5-diphenylpenta-1,4-dien-3-one (7·06 g, 30 mmol) in hot ethanol (500 ml) and sodium acetate (0·250 g) in water (2 ml) was added dropwise under nitrogen to a stirred hot solution of K_2PtCl_4 (4·16 g, 10 mmol) in water (250 ml). After 24 h under reflux, dark purple-black crystals, a mixture of $Pt(dpo)_2$ and $Pt(dpo)_3$, were filtered from the warm solution.

The solid product was purified of excess of dpo by washing with acetone, then extracted with successive 200 ml portions of hot CH_2Cl_2. Gentle reflux of the combined extracted solutions for 30 min effected near quantitative conversion of the three-co-ordinate derivative to $Pt(dpo)_2$ with elimination of one mole of free ligand. Upon evaporation of this solution, the resultant dark purple residue was extracted several times with acetone, before pure purple $Pt(dpo)_2$ (3·10 g, 47%) was filtered off and dried.

Preparation of $Pt(dpo)L_2$ *and Derivatives*.—(a) From $Pt(dpo)_2$, reaction (*i*) (Scheme). (i) For L = PPh_3, $Pt(dpo)_2$ (0·332 g, 0·5 mmol) in toluene (10 ml) was reacted in a sealed evacuated Carius tube with triphenylphosphine (0·262 g, 1 mmol) for 12 h at 25°. The initial purple solution became amber after 2 h. Upon evaporation of volatile materials, yellow crystals of $Pt(dpo)L_2$ (0·450 g) precipitated on cooling. The solid product was filtered off and washed with cold diethyl ether. 1,5-Diphenylpenta-1,4-dien-3-one was isolated in quantitative yield from evaporation of the filtrate solution and the ether washings. Molecular weight 937, calc. 954. I.r. absorptions in $CHCl_3$ were typical for the series $Pt(dpo)L_2$: ν(CO) 1652s cm^{-1} (*cf.* 1652m-s for free dpo); ν(C=C) free 1603vs (*cf.* 1621 cm^{-1}); ν(C=C) co-ordinated <1480 cm^{-1} (ref. 10).

(ii) $Pt(dpo)L_2$ was the sole product isolated from similar

---

[13] Y. Takahashi, T. Ito, S. Sakai, and Y. Ishii, *J. Chem. Soc.* (*D*), 1970, 1065.

[14] E. O. Graves, C. J. L. Lock, and P. M. Maitlis, *Canad. J. Chem.*, 1968, **46**, 3879.

[15] W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1968, 1278.

[16] C. D. Cook and K. Y. Wan, *Inorg. Chem.*, 1971, 2696.

[17] M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2525.

[18] R. D. W. Kemmitt and R. D. Moore, *J. Chem. Soc.* (*A*), 1971, 2472.

[19] H. D. Empsall, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 96, and series.

reactions for the molar proportions $n\mathrm{PPh_3} : \mathrm{Pt(dpo)_2}$ where n = 4, 6, and 10.

(iii) For L = $\mathrm{AsPh_3}$ and n = 2, reaction as above (with more decomposition) yielded orange $\mathrm{Pt(dpo)L_2}$, recrystallized from diethyl ether–hexane after chromatographic separation (elution with $\mathrm{CH_2Cl_2}$ from a Florisil column) of dpo from the oily product residue.

(iv) For L = $\mathrm{AsPh_3}$ and $n \geqslant 4$, $\mathrm{PtL_4}$ was filtered from solution as the major product, identified by its physical properties and i.r. spectrum.

(v) For L = $\mathrm{PEt_3}$ and $\mathrm{AsEt_3}$ and for n = 2 and 4, reaction as above gave an amber solution with some insoluble dark decomposition product. Upon filtration and evaporation of volatile material, chromatography of the amber oily residue on a Florisil column with elution by $\mathrm{CH_2Cl_2}$ yielded free dpo from the first yellow fraction collected, and pure $\mathrm{Pt(dpo)L_2}$ from the second. The product for L = $\mathrm{PEt_3}$ was recrystallized slowly from diethyl ether–hexane at −70° while the analogous derivative for L = $\mathrm{AsEt_3}$ was isolated as an amber oil. The stoicheiometries of these products were confirmed by intensity ratios for n.m.r. absorptions corresponding to phenyl protons and one free double bond (12), one co-ordinated double bond (2) and ligand ethyl protons (30). However for n = 2 and L = $\mathrm{PEt_3}$ some evidence was found for a second related product which could not be satisfactorily isolated.

(vi) Reaction and work-up as above for L = $\mathrm{PPh_2Me}$ yielded yellow solid $\mathrm{Pt(dpo)L_2}$ recrystallized from diethyl ether–hexane at −70°. An n.m.r. spectrum of the product confirmed the *cis*-orientation of the phosphine ligands; ^2J(PH) 8, ^3J(PtH) 31 Hz.

(b) From $\mathrm{Pt(PPh_3)_4}$, reaction (*iii*) (Scheme). (i) A solution of $\mathrm{Pt(PPh_3)_4}$ (0·312 g, 0·25 mmol) and dpo (0·059 g, 0·25 mmol) in toluene was shaken in an evacuated Carius tube for 15 h at 60°. After evaporation of volatile material, the amber oily residue was dissolved in diethyl ether from which yellow crystals of $\mathrm{Pt(dpo)(PPh_3)_2}$ (0·210 g) separated on standing. The product was filtered off, washed with cold diethyl ether, then dried. All physical and spectroscopic properties were identical to those of the derivative isolated by reaction (*i*) for L = $\mathrm{Ph_3P}$.

(ii) Similar products were obtained for molar proportions $\mathrm{PtL_4} : n$ dpo where $n = \frac{1}{2}$, 4, and 10. For $n = \frac{1}{2}$, some unreacted platinum complex was recovered and no evidence was found for metal co-ordination to a single unit of dpo at both olefinic sites.

(iii) Reactions as above with 4-phenylbut-3-en-2-one (ba) and 1,3-diphenylprop-2-en-1-one (bap) for n = 1 afforded off-white solid $\mathrm{Pt(ba)(PPh_3)_2}$ and $\mathrm{Pt(bap)(PPh_3)_2}$, crystallized from diethyl ether by the addition of hexane. Spectroscopic properties were qualitatively similar to those for $\mathrm{Pt(dpo)(PPh_3)_2}$.

Reactions of $\mathrm{Pt(dpo)L_2}$ *with Olefins and Acetylenes* (OL), *Scheme, Reaction* (ii).—(a) *For* L = $\mathrm{Ph_3P}$. (i) OL = $\mathrm{C_2Cl_4}$. $\mathrm{Pt(dpo)L_2}$ (0·300 g) in dry toluene was reacted with distilled $\mathrm{C_2Cl_4}$ (2 ml) for 24 h at 75° in a sealed evacuated Carius tube. After evaporation of volatile material and extraction of the residue with diethyl ether, white solid $\mathrm{Pt(C_2Cl_4)L_2}$ (0·260 g) was filtered from solution and recrystallized from dichloromethane–hexane. The product, identical to that obtained under similar conditions from the reaction of $\mathrm{PtL_4}$ with $\mathrm{C_2Cl_4}$, was identified by its physical and spectroscopic properties.[15]

Only starting materials were recovered from the reverse reaction of $\mathrm{Pt(C_2Cl_4)L_2}$ with an excess of dpo.

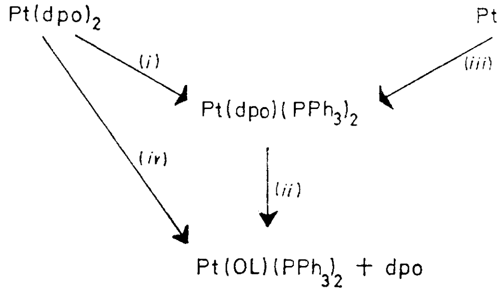
(ii) As above, $\mathrm{Pt(C_2Cl_4)L_2}$ was obtained in high yield from reactions of $\mathrm{Pt(ba)L_2}$ and $\mathrm{Pt(bap)L_2}$ with $\mathrm{C_2Cl_4}$.

(iii) OL = $\mathrm{(CF_3)_2CO}$ and $\mathrm{CF_3C{\equiv}CCF_3}$. Similar reactions with hexafluoroacetone or hexafluorobut-2-yne (3 atm) afforded $\mathrm{Pt[(CF_3)_2CO]L_2}$ and $\mathrm{Pt(CF_3C{\equiv}CCF_3)L_2}$ respectively, isolated as above. Products were identified by comparison of physical and spectroscopic properties to those reported for these derivatives.[14,20]

(iv) OL = $\mathrm{CS_2}$. Similarly, $\mathrm{Pt(CS_2)L_2}$ was isolated from the reaction with purified $\mathrm{CS_2}$ (5 ml).

(v) OL = $\mathrm{C_2H_4}$. Under a range of reaction conditions, including addition of an excess of $\mathrm{PPh_3}$, the analogous derivative $\mathrm{Pt(C_2H_4)L_2}$ could not be isolated from the reaction of $\mathrm{Pt(dpo)L_2}$ with $\mathrm{C_2H_4}$.

(vi) Reaction with $\mathrm{Br_2}$. $\mathrm{Pt(dpo)L_2}$(0·200 g) in toluene (10 ml) was shaken with bromine (0·5 ml) for 3 days at 25° in a sealed evacuated Carius tube. A pale yellow solid identified as $\mathrm{PtBr_2L_2}$ was filtered from solution and identified by its m.p. and i.r. spectrum. Free dpo (0·043 g) was recovered in quantitative yield from the filtrate solution.



(I)

SCHEME Preparation of platinum–π-olefin complexes; (*i*), L = $n\mathrm{PPh_3}$ in benzene, n = 2—10; (*ii*) OL = $\mathrm{C_2Cl_4}$, $\mathrm{(CF_3)_2CO}$, *etc.*; (*iii*), dpo in toluene; (*iv*) 2 $\mathrm{PPh_3}$ with an excess of OL in toluene

(b) *For* L = $\mathrm{AsPh_3}$. (i) As above for L = $\mathrm{AsPh_3}$ and OL = $\mathrm{C_2Cl_4}$, reaction yielded the appropriate olefin derivative, recrystallized as the solvated complex $\mathrm{Pt(C_2Cl_4)(AsPh_3)_2,2CH_2Cl_2}$ from dichloromethane–diethyl ether at −20°.

(c) *For* L = $\mathrm{PEt_3}$. (i) OL = $\mathrm{CF_3C{\equiv}CCF_3}$. $\mathrm{Pt(dpo)L_2}$ (0·332 g) in dry toluene was reacted with hexafluorobut-2-yne (3 atm) for 48 h at 25° in a sealed evacuated Carius tube. The amber liquid slowly became pale yellow, and a colourless oil separated from solution. After evaporation of volatile material, components of the residue were separated by chromatography on a Florisil column with elution by $\mathrm{CH_2Cl_2}$. $\mathrm{Pt(CF_3C{\equiv}CCF_3)(PEt_3)_2}$ (0·270 g), obtained from the first fraction, was purified by sublimation at 80°. The ^{19}F n.m.r. spectrum consisted of a doublet centred at 54·3 p.p.m. from $\mathrm{CFCl_3}$ [^4J(PF) 11 Hz] with accompanying doublet sidebands [^3J(PtF) 65·5 Hz]. Identity was confirmed by elemental analysis and an i.r. spectrum with ν(C≡C) 1771 cm^{-1}.

(ii) OL = $\mathrm{C_2F_4}$. $\mathrm{Pt(C_2F_4)(PEt_3)_2}$ (0·090 g) was isolated as above from the reaction of $\mathrm{Pt(dpo)L_2}$ with $\mathrm{C_2F_4}$. For this product, a ^{19}F n.m.r. spectrum with resonance centred at 127·5 p.p.m. from $\mathrm{CFCl_3}$ and ^2J(PtF) 280 Hz was similar to the $\mathrm{X_2AA'X'_2}$ pattern reported [17] for the known analogue where L = $\mathrm{PPh_3}$.

---

[20] B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 167.

(iii) OL = C_2Cl_4. A similar reaction of Pt(dpo)L_2 with C_2Cl_4 proceeded with pronounced decomposition affording a low yield of Pt(C_2Cl_4)L_2.

(iv) OL = $(CF_3)_2CO$. Pt(dpo)L_2 (0·350 g) in dried toluene was shaken with an excess of hexafluoroacetone (6 atm) for 48 h at 25°. After 3 h the initially amber solution became pale yellow. Upon evaporation of volatile material, the yellow oily residue was purified by chromatography on a Florisil column with elution by dichloromethane. The first fractions contained a white solid, m.p. 146—147° (0·175 g) which was recrystallized from diethyl ether–hexane and purified further by t.l.c. with toluene–ethyl acetate (10 : 1). An i.r. spectrum of this product showed bands corresponding to dba and triethylphosphine as well as strong C–F absorptions. A ^1H n.m.r. spectrum contained absorptions at τ 2·8 (m, 11H), τ 4·8 (d, 1H), τ 6·15 (d, 1H), τ 6·45 (br, 1H), τ 8·1, 8·8 (m,m *ca.* 60H) while the ^{19}F spectrum in $(CD_3)_2CO$ consisted of three broadened quartets [*J*(FF) 10 Hz] 68·9, 71·7, and 72·8 p.p.m. from $CFCl_3$, one quartet of doublets [*J*(FF) 10, *J*(HF) 3 Hz] at 73·4 p.p.m., and a sharp singlet corresponding to free hexafluoroacetone. The product was stable in the solid state although initially colourless solutions in *e.g.* $(CD_3)_2CO$ slowly turned yellow with the evolution of gas. Elemental analysis, mass spectral evidence, and n.m.r. data suggest a structure of stoicheiometry Pt_2(dpo)$\{(CF_3)_2CO\}L_4$ involving cyclization of hexafluoroacetone with co-ordinated dpo. The exact nature of this product could not be conclusively determined. No evidence was found for the formation of Pt$\{(CF_3)_2CO\}L_2$ by this procedure.

(v) OL = $(CF_3)_2CNH$. A white crystalline solid, isolated as above for OL = $(CF_3)_2CNH$, proved to be partially soluble in $CDCl_3$. Both ^1H and ^{19}F n.m.r. spectra of the soluble fraction resembled those for the cyclization product with $(CF_3)_2CO$ while the solution also yellowed with time. A ^1H n.m.r. spectrum of the insoluble fraction in C_6D_6 showed only triethylphosphine absorptions while the ^{19}F spectrum consisted of a triplet (separation 42 Hz) of doublets (separation 5 Hz) at 62·3 p.p.m. from $CFCl_3$ and a closely spaced doublet (separation 3 Hz) at 79·7 p.p.m. with integrals in the ratio 1 : 1. Elemental analysis of this product was consistent with the stoicheiometry Pt$\{(CF_3)_2CNH\}_2L_2$. I.r. spectra of both samples showed strong C–F absorptions, however, their identities could not be unambiguously determined.

Reactions of Pt(dpo)$_2$ *directly with* PPh_3 *and Olefin, Scheme, Reaction* (iv).—(i) Pt(dpo)$_2$ (0·332 g, 0·5 mmol) in toluene solution was reacted with PPh_3 (0·262 g, 1 mmol) and distilled C_2Cl_4 (2 ml) for 24 h at 45° in a sealed evacuated Carius tube. Pt(C_2Cl_4)$(PPh_3)_2$ (0·380 g) was isolated as previously reported.

(ii) No reaction was observed between Pt(dpo)$_2$ and C_2Cl_4 under similar conditions in the absence of triphenylphosphine.

We thank Johnson, Matthey and Co. Ltd. for the loan of platinum salts and the National Research Council of Canada for the award of a post-doctoral fellowship to W. J. C.

[3/2270 *Received, 5th November,* 1973]