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REACTIONS OF (π-1,5-CYCLOOCTADIENE)ORGANOPLATINUM(II)COMPOUNDS AND THE SYNTHESIS OF PERFLUOROALKYLPLATINUM COMPLEXES

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SUMMARY

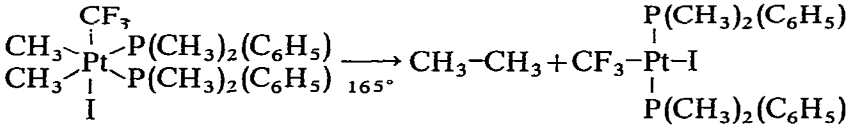
An improved synthesis for the complexes $PtR_2(COD)$, [where COD = 1,5-cyclooctadiene, R = I, CH_3, C_2H_5, $CH_2C_6H_5$, $CH_2Si(CH_3)_3$, C_6H_5] and the reactions with HCl (generated *in situ*) to give PtRCl(COD) are described. The coupling constant J(Pt–H) to the olefinic carbons varies with the *trans*-influence of the *trans*-ligand. Displacement of COD from $Pt(CH_3)_2(COD)$ by L (where L = isocyanide, phosphine, amine, bipyridyl and trimethylarsine) gave a series of compounds *cis*-$Pt(CH_3)_2L_2$. The oxidative addition of methyl iodide to $PtR_2(COD)$(R = CH_3, CH_2CH_3) gave the platinum(IV) compounds $[Pt(CH_3)_3I]_4$ and $[Pt(CH_3)(CH_2CH_3)_2I]_4$. Diethylmethylplatinum(IV) iodide reacted with 4-methylpyridine (γ-Pic) to give $Pt(C_2H_5)_2(CH_3)(\gamma\text{-Pic})_2I$ and with $AgClO_4$ and pyridine to give $[Pt(C_2H_5)_2(CH_3)(NC_5H_5)_3](ClO_4)$. The reaction of $R_2Pt(COD)$ (R = CH_3 and C_2H_5) with iodine or bromine gave the Pt^{IV} compounds $[PtR_2X_2]_x$. Several reactions of these compounds are discussed. The NMR spectrum of $Pt(CH_3)_2(CNC_2H_5)_2Br_2$ is unusual in that coupling of the ^{14}N nucleus with the ethyl hydrogens is observed. The reaction of acetyl chloride with $Pt(CH_3)_2(COD)$ gave the Pt^{IV} compound $[Pt(CH_3)_2(COCH_3)Cl]_4$. Further reaction of γ-picoline with the acyl compound gave 2 isomers of $Pt(CH_3)_2(COCH_3)(\gamma\text{-Pic})_2Cl$ as predicted by cleavage of a cubane-type structure. The reaction of iodine with $PtR_2(COD)$(R = $CH_2C_6H_5$) gave a mixture of $[PtR_2I_2]_x$ and PtRI(COD), whereas for R = $CH_2Si(CH_3)_3$ only PtRI(COD) was obtained. The possible mechanisms for these reactions are discussed. Trifluoromethyl iodide reacted with $Pt(CH_3)_2(COD)$ to give $Pt(CF_3)_2(COD)$ and displacement reactions of COD with ligands L, [where L = CNC_2H_5, $P(CH_3)_2(C_6H_5)$, $As(CH_3)_3$, Bipy, γ-Pic, $Sb(C_6H_5)_3$, $As(C_6H_5)_3$, $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ and $(CH_3)_2NCH_2CH_2N(CH_3)_2$] gave a series of compounds *cis*-$Pt(CF_3)_2L_2$. Oxidative addition reactions with iodine and the stereochemistry of the resultant Pt^{IV} compounds are described.

INTRODUCTION

Although a large number of organoplatinum compounds have been prepared, most have contained phosphines or arsines as stabilizing ligands[1]. Similar complexes with other ligands such as isocyanides and amines have not been prepared, presumably because a competitive reaction occurs during the attempted syntheses, involving interaction of the organolithium or Grignard reagent with the ligand itself. In this paper we describe a convenient preparative route to several types of organoplatinum compounds.

Since the preparation of tetrameric trimethylplatinum(IV) iodide in 1909[2,3] only two other similar platinum(IV) compounds have been prepared, and only then with some difficulty. Thus, $[Pt(CH_3)_2Br_2]_x$ was prepared[4] from $[Pt(CH_3)_3I]_4$ after refluxing for eight hours in bromine and concentrated hydrobromic acid, while triethylplatinum(IV) chloride[5] was prepared in 30% yield by the reaction of diethylmercury with platinum tetrachloride. We now describe a very convenient preparation of $[Pt(CH_3)_2X_2]_2$ and $[Pt(CH_3)_3I]_4$ as well as the synthesis of four similar new Pt^{IV} compounds. Several reactions of these compounds are discussed as well as the mechanism of their formation from Pt^{II} compounds.

The syntheses of perfluoroalkylmetal complexes pose interesting synthetic challenges to organometallic chemists particularly since short chain perfluoroalkyllithium or Grignard compounds are not suitable synthetic reagents[6]. Many platinum(IV) perfluoroalkyl compounds have been prepared by conventional oxidative addition reactions[7,8] and the pyrolysis of some of these compounds has led to the synthesis of CF_3–platinum(II) compounds containing phosphines or arsines (eqn. 1).



$$(CH_3)_2\underset{I}{\overset{CF_3}{Pt}}[P(CH_3)_2(C_6H_5)]_2 \xrightarrow[165^\circ]{} CH_3\text{–}CH_3 + CF_3\text{–}\underset{P(CH_3)_2(C_6H_5)}{\overset{P(CH_3)_2(C_6H_5)}{Pt}}\text{–}I \qquad (1)$$

We now report a general route[9] to a variety of bis(trifluoromethyl)platinum(II) and -platinum(IV) compounds.

RESULTS AND DISCUSSION

A. Syntheses of $PtR_2(COD)$, and $PtRCl(COD)$

Attempts to prepare $Pt(COD)I_2$ from K_2PtCl_6 according to the method published by Doyle[10] have been unsuccessful. A better method, outlined in the Experimental section, is rather time-consuming (2 days) but gives pure $Pt(COD)Cl_2$ in good yield; metathetical replacement of the chloride with iodine then proceeds quantitatively. The dimethyl[10], diethyl[10], and diphenyl[10] and bis(trimethylsilyl)methyl[11] complexes have been prepared previously; however, our procedures gave improved yields. The dibenzyl complex is new and was isolated as stable white crystals.

Platinum(II)–carbon bonds are very susceptible to attack by mineral acids[1]; conversion to a platinum(II) halide occurs readily on the addition of a molar equivalent of HCl in ether. However, such reactions are difficult to control due to problems of standardizing the ether solution and maintaining its concentration. The addition *in situ* of the appropriate amount of acetyl chloride to a dichloromethane/methanol solution greatly simplifies this hydrohalogenation reaction, and facilitates the generation of the milligram amounts of HCl necessary for the small scale synthesis in good yield of the complexes PtRCl(COD), where $R=CH_3$, C_6H_5, $CH_2C_6H_5$.

The ^1H NMR spectra of these complexes (Table 1) shows resonances typical of

TABLE 1

^{1}H NMR DATA^{a} FOR ORGANOPLATINUM(II) 1,5-CYCLOOCTADIENE COMPLEXES

Complex	*Cyclooctadiene resonances*			*Other resonances*
	δ(CH)	*J(Pt–H)*	*δ(CH$_2$)*	
$Pt(CH_3)_2(COD)$	4.65	40	2.15	$\delta(Pt\text{–}CH_3)$ 0.58, $^2J(Pt\text{–}H)$ 83.4
$Pt(C_6H_5)I(COD)$	5.80	33	2.41	
	4.72	74		
$Pt(CH_3)Cl(COD)$	5.52	35	2.37	$\delta(Pt\text{–}CH_3)$ 0.89, $^2J(Pt\text{–}H)$ 72.0
	4.50	78	2.30	
$Pt(C_6H_5)Cl(COD)$	5.82	33	2.48	
	4.63	77		
$Pt(CH_2C_6H_5)_2(COD)$	4.59	41	1.75	$\delta(Pt\text{–}CH_2)$ 3.28, $^2J(Pt\text{–}H)$ 114
$Pt(CH_2C_6H_5)Cl(COD)$	5.59	36	2.30	$\delta(Pt\text{–}CH_2)$ 3.13, $^2J(Pt\text{–}H)$ 102
	4.31	74		
$Pt(CH_2C_6H_5)I(COD)$	5.54	35	1.50	$\delta(Pt\text{–}CH_2)$ 3.90, $^2J(Pt\text{–}H)$ 105
	3.21	73		
$Pt[CH_2Si(CH_3)_3]I(COD)$	5.37	39	1.60	$\delta(Pt\text{–}CH_2)$ 1.72, $^2J(Pt\text{–}H)$ 78
	4.29	71		$\delta(Si\text{–}CH_3)$0.44
$Pt(C_2H_5)_2(COD)$	4.76	38	1.90	$\delta(Pt\text{–}CH_2)$ 1.87, $^2J(Pt\text{–}H)$ 92.2, $\delta(Pt\text{–}C\text{–}CH_3)$ 1.52, $^3J(Pt\text{–}H)$ 80.5

[a] Spectra were recorded on $CHCl_3$ solutions, chemical shifts (δ) are in ppm downfield from TMS and coupling constants (J) are given in Hz, COD 1,5-cyclooctadiene.

the organo group as well as two distinct resonances for the olefinic hydrogens. The high field peak shows a significant coupling to ^{195}Pt ($I=\frac{1}{2}$, 34% natural abundance) [$J(Pt\text{–}H)\approx 75\text{–}80$ Hz] and is assigned to the olefinic group *trans* to chloride while the other resonance with $J(Pt\text{–}H)\approx 40$ Hz is assigned to the group *trans* to R. The methylene resonances were complex and no attempt was made to extract platinum coupling constants from the spectra.

B. Displacement reactions

The cyclooctadiene in $Pt(CH_3)_2(COD)$ is strongly bonded to platinum due to the presence of the strongly electron-donating methyl groups which enlarge the Pt 5*d* orbitals allowing greater overlap with the olefinic π^* orbitals and synergistically strengthening the Pt–(COD) bond. Consequently, displacement of COD is difficult and high temperatures are required for ligands of low *trans*-influence. However for ligands of high *trans*-influence the reaction is usually complete within one hour. A number of phosphine, arsine and stibine complexes have been prepared by Kistner *et al.*[12], and we have extended these displacement reactions as shown in eqn. (2). ^{1}H NMR data for the new complexes are given in Table 2.

$$Pt(CH_3)_2(COD)+2\,L \xrightarrow[80°;\,1\,h]{} cis\text{-}Pt(CH_3)_2L_2+COD \qquad (2)$$

$L = p\text{-}CNC_6H_4CH_3, CNC_2H_5, P(p\text{-tolyl})_3, As(CH_3)_3$, Bipy*, $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$, $(CH_3)_2NCH_2CH_2N(CH_3)_2$. Of particular interest are the two isocyanide

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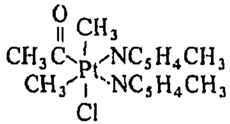
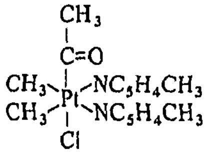
* $Pt(CH_3)_2$Bipy was first prepared by R. J. Puddephatt[13].

TABLE 2

^{1}H NMR DATA[a] FOR ORGANOPLATINUM COMPLEXES

Complex	*δ(Pt–CH₃)*	*²J(Pt–CH₃)*	*Other resonances and coupling constants*
$Pt(CH_3)_2(CNC_6H_4CH_3)_2$	0.74	74.6	$\delta(CH_3)$ 2.34
$Pt(CH_3)_2[P(p\text{-}C_6H_4CH_3)_3]_2$	0.30	69.0	$\delta(CH_3)$ 2.32
$[Pt(CH_3)_2]_2(DPPA)_2$	0.49	74.0	
$Pt(CH_3)_2(CNC_2H_5)_2$	0.30	75.0	$\delta(CH_3)$ 1.31, $\delta(CH_2')$ 3.45, $J(H\text{-}H')$ 7.0
$Pt(CH_3)_2[(CH_3)_2NCH_2CH_2N(CH_3)_2]$	0.19	86.0	$\delta(NCH_3)$ 2.59, $^3J(Pt\text{-}H)$ 22.7, $\delta(NCH_2)$ 2.57, $^3J(Pt\text{-}H)$ 12.2
$Pt(CH_3)Cl(CNC_6H_4CH_3)_2$	0.91	61.4	$\delta(CH_3)$ 2.39
$Pt(CH_3)Cl$ Bipy	1.09	79.4	
$[Pt(CH_3)$ Bipy $(NCC_6H_4OCH_3)](PF_6)$	1.06	80.4	$\delta(OCH_3)$ 2.57
$Pt(CH_3)_2(CNC_2H_5)_2Br_2$	1.66	64.8	$\delta(CH_3)$ 1.48, $^3J(^1H\text{-}^{14}N)$ 2.8 $\delta(CH_2')$ 3.89, $^2J(^1H\text{-}^{14}N)$ 1.0 } $J(H\text{-}H')$ 7.2
$Pt(CH_3)_2(COCH_3)Cl$	1.66	85.4	$\delta(COCH_3)$ 2.43, $^3J(Pt\text{-}H)$ 15.6
	1.21[b]	74.2	$\delta(COCH_3)$ 2.43, $^3J(Pt\text{-}H)$ 8.0
	1.41[c]	71.0	$\delta(CH_3)$ 2.42
	1.32	72.0	$\delta(COCH_3)$ 2.17, $^3J(Pt\text{-}H)$ 16.0 $\delta(CH_3)$ 2.42
$Pt(CH_3)(C_2H_5)_2I$	1.54	81.4	$\delta(Pt\text{-}CH_2)$ 2.33, $^2J(Pt\text{-}CH)$ 78.8 $\delta(Pt\text{-}C\text{-}CH_3)$ 0.87, $^3J(PtCCH_3)$ 81.9 } $J(H\text{-}H')$ 7.6
$[Pt(CH_3)(C_2H_5)_2(NC_5H_5)_3](ClO_4)$	1.23	71.8	$\delta(PtCH_2)$ 2.01, $^2J(Pt\text{-}CH_2)$ 79.4 $\delta(Pt\text{-}C\text{-}CH_3)$ 0.58, $^3J(Pt\text{-}C\text{-}CH_3)$ 57.0 } $J(H\text{-}H')$ 7.6
$Pt(C_2H_5)_2(4\text{-}CH_3C_5H_4N)_2I_2$			$\delta(PtCH_2')$ 4.21, $^2J(Pt\text{-}CH_2)$ 87.0, $J(H\text{-}H')$ 7.6 $\delta(Pt\text{-}CCH_3)$ 1.25, $^3J(PtCCH_3)$ 29.2, $\delta(4\text{-}CH_3)$ 1.64

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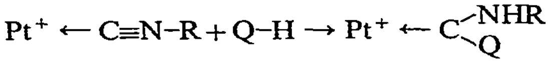
[a] Spectra were recorded in CH_2Cl_2 or $CHCl_3$ solutions. Chemical shifts (δ) are in ppm downfield from $Si(CH_3)_4$ and coupling constants (*J*) are given in Hz; Bipy 2,2′-Bipyridine; DPPA 1,2-bis(diphenylphosphino)acetylene. [b] *Trans* to chloride. [c] *Trans*- to 4-methylpyridine.

complexes. Organometallic isocyanide complexes are susceptible to reaction at the C≡N bond by organolithium compounds[14], and hence these two platinum–isocyanide complexes cannot be prepared by the action of lithio or Grignard reagents on the platinum(II) dihalide–isocyanide complexes. In previous papers we examined the reactivity of isocyanide complexes towards various protic nucleophiles to give "carbene" complexes [eqn. (3)]



$$\mathrm{Pt^+ \leftarrow C{\equiv}N{-}R + Q{-}H \rightarrow Pt^+ \leftarrow C}\begin{matrix}\nearrow \mathrm{NHR} \\ \searrow \mathrm{Q}\end{matrix} \qquad (3)$$

$$\mathrm{Q = R'NH-,\ R'O-,\ R'S-}$$

It was suggested that nucleophilic attack at the isocyanide was facilitated by increasing the electron density on platinum [reflected by lowering $\Delta\nu$(N≡C)]. The Raman N≡C stretching frequency in *cis*-$Pt(CH_3)_2(CNC_6H_4CH_3)_2$ is 2139 cm^{-1}, an increase on coordination of only 14 cm^{-1} over that of the free isocyanide. Although this compound should thus be a prime candidate for carbene formation, there was no tendency for the complex to react with aniline derivatives bearing electron-donating *para*-substituents[16]. Carbene formation is usually thermodynamically favorable (the reactions being exothermic[17]) since the carbenes are excellent σ-donors[18] and thus increase the electron density on the metal. We have recently examined[8], kinetically, oxidative addition reactions of $Pt(CH_3)_2(CNC_6H_4CH_3)_2$ and the low activation energies indicate that the platinum atom in this compound is already very electron rich. If the electron density on platinum is a critical factor, the fact that carbene formation from $Pt(CH_3)_2(CNC_6H_4CH_3)_2$ does not occur is therefore understandable. This may also be the reason that no zerovalent transition metal carbenes, derived from isocyanides, [where $\Delta\nu$(N≡C) is negative] have been synthesized. Interestingly, *cis*-$Pt(CH_3)_2(CNC_6H_4CH_3)_2$ reacted readily with a molar equivalent of hydrogen chloride to give the *cis*-isomer of $Pt(CH_3)Cl(CNC_6H_4CH_3)_2$, even though most complexes of the type $Pt(CH_3)ClL_2$ are *trans*[1] (*cf.* *cis*-$Pt(CH_3)Cl(CNC_6H_4CH_3)[P(CH_3)_2(C_6H_5)]$[15b]). (COD)$Pt(C_6H_5)_2$ also reacted with two moles of isocyanide to displace 1,5-cyclooctadiene, giving *cis*-$Pt(C_6H_5)_2(CNC_6H_4CH_3)_2$.

Although the 1,5-cyclooctadiene in $Pt(CH_3)Cl(COD)$ is strongly bonded, refluxing with bipyridyl in dichloromethane for 30 min gave $Pt(CH_3)ClBipy$ in nearly quantitative yields. The chloride was removed in the presence of a neutral ligand by $AgPF_6$, exemplified by the reaction with *p*-methoxybenzonitrile [eqn. (4)].

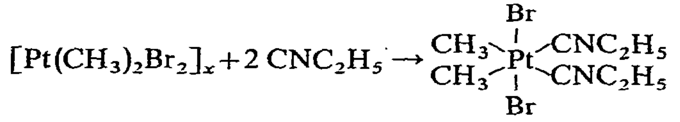
$$cis\text{-}\mathrm{Pt(CH_3)ClBipy + AgPF_6 + }p\text{-}\mathrm{NCC_6H_4OCH_3} \xrightarrow[-\mathrm{AgCl}]{\mathrm{Acetone}}$$
$$cis\text{-}[\mathrm{Pt(CH_3)Bipy(NCC_6H_4OCH_3)}]^+\mathrm{PF_6^-}$$

Similarly, as a result of the lability of the chloride in PtRCl(COD) ($R = CH_3$, C_6H_5, $CH_2C_6H_5$), other series of cationic complexes may be prepared. The cyclooctadiene is readily displaced from these cations by neutral and anionic ligands and such reactions will be described elsewhere[19].

C. Reactions of PtR_2*(COD)*

To date, there have been no reports of stable olefin and acetylene complexes of Pt^{IV}, although they have been suggested as reaction intermediates[20–22]. In an attempt to prepare $Pt(CH_3)_3(COD)I$ by the addition of methyl iodide to $Pt(CH_3)_2(COD)$, we found that oxidative addition occurred; however cyclooctadiene was displaced to give $[Pt(CH_3)_3I]_4$ in good yield. The relative ease of oxidation of $Pt(CH_3)_2(COD)$ with the elimination of cyclooctadiene prompted us to investigate this reaction as a possible source for a variety of new organoplatinum(IV) compounds.

$Pt(CH_3)_2(COD)$ reacted immediately with bromine or iodine in dichloromethane or ether to give $[Pt(CH_3)_2X_2]_x$ in nearly quantitative yields. The compounds precipitate from solution as powders which are insoluble in organic solvents. They were characterized by elemental analysis and reaction with ethyl isocyanide as shown in eqn. (5).



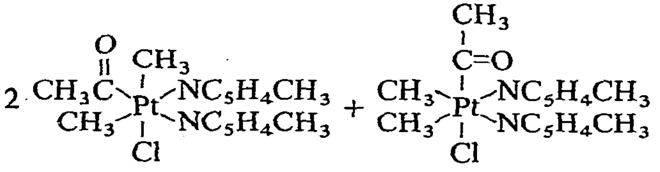
$$[Pt(CH_3)_2Br_2]_x + 2\,CNC_2H_5 \rightarrow (CH_3)_2PtBr_2(CNC_2H_5)_2 \qquad (5)$$

(I)

The NMR spectrum of (I) (Table 2) is unusual in that the ethyl protons of the isocyanide are coupled to the ^{14}N nucleus ($I=1$, 99.635% natural abundance) splitting each peak into a 1/1/1 "triplet". In most ethyl isocyanide complexes[15,21,22] the ethyl resonances are broadened as a result of a relaxation process associated with the interaction of the ^{14}N quadrupole with the large electric field gradients within the molecule[23]. However in the present case, as for the free isocyanide the electric field gradients surrounding the ^{14}N nucleus must be small and the quadrupolar relaxation is diminished. The measured $^{14}N-^{1}H$ couplings (Table 2) are interesting since the β-coupling is larger than the α-coupling.

Acetyl chloride reacted with $Pt(CH_3)_2(COD)$ to give the acyl compound $[Pt(CH_3)_2(COCH_3)Cl]_x$ which is probably tetrameric as are all other such platinum complexes[24]. The reaction of two molar equivalents of γ-picoline with $[Pt(CH_3)_2(COCH_3)Cl]_x$ gave a product with empirical formula $Pt(CH_3)_2(COCH_3)(\gamma\text{-Pic})_2Cl$. The NMR spectrum in chloroform (Table 2) showed the presence of three methyl groups of equal intensity and only two acyl peaks in the ratio of 2/1. These results and the various Pt–H coupling constants are consistent with the presence of two isomers in the ratio of 2/1, as predicted for the cleavage of a cubane type structure with bridging chlorides [eqn. (6)].

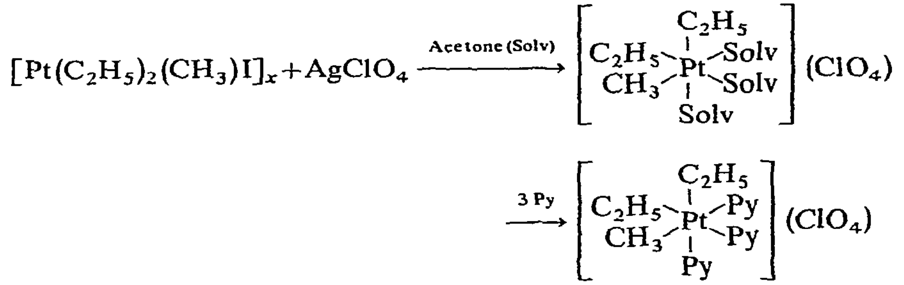
$$[Pt(CH_3)_2(COCH_3)Cl]_4 + 2\,NC_5H_4CH_3 \rightarrow$$



$$2\,(CH_3C(O))(CH_3)_2PtCl(NC_5H_4CH_3)_2 + (CH_3)_2(CH_3C{=}O)PtCl(NC_5H_4CH_3)_2 \qquad (6)$$

No reaction occurred between $Pt(CH_3)_2(COD)$ and ethyl iodide or benzoyl chloride.

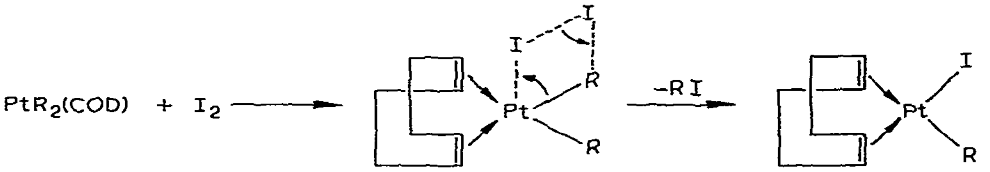
$Pt(C_2H_5)_2(COD)$ reacted readily with methyl iodide and iodine to give the two new platinum(IV) compounds $[Pt(C_2H_5)_2(CH_3)I]_x$ and $[Pt(C_2H_5)_2I_2]_x$ (where x is probably four). The addition of two molar equivalents of γ-picoline to $[Pt(C_2H_5)_2I_2]_x$ gave golden crystals of $Pt(C_2H_5)_2(\gamma\text{-Pic})_2I_2$. Similarly, $[Pt(C_2H_5)_2(CH_3)I]_x$ reacted with pyridine to give white crystals of $Pt(C_2H_5)_2(CH_3)(NC_5H_5)_2I$; however, the NMR spectrum was exceedingly complicated as might be expected for a mixture of isomers. For $[Pt(C_2H_5)_3I]_4$ the values of $^2J(Pt-CH_2)$ and $^3J(Pt-CH_3)$ have opposite signs, as observed for other ethyl-metal complexes[25,26]. Similarly, for $[Pt(C_2H_5)_2(CH_3)I]$, irradiation of the low field ^{195}Pt satellite of the CH_2 resonance caused the high field satellite of the $-CH_3$ peak to collapse, indicating opposite signs for these two platinum coupling constants. The iodide in $[Pt(C_2H_5)_2(CH_3)I]_x$ may be removed by the addition of a silver salt of a non-coordinating anion, *e.g.* $AgClO_4$, in acetone or methanol to give a stable solvent cation.



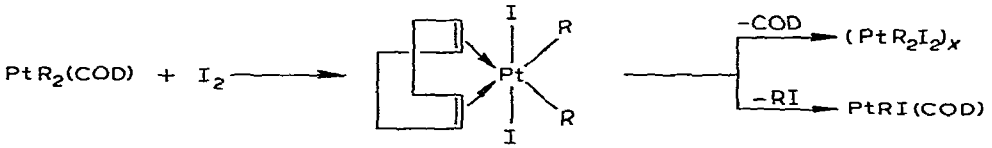
$$[Pt(C_2H_5)_2(CH_3)I]_x+AgClO_4 \xrightarrow{\text{Acetone (Solv)}} \left[\begin{array}{c} C_2H_5 \\ C_2H_5\diagdown\ |\ \diagup Solv \\ Pt \\ CH_3\diagup\ |\ \diagdown Solv \\ Solv \end{array}\right](ClO_4) \xrightarrow{3\,Py} \left[\begin{array}{c} C_2H_5 \\ C_2H_5\diagdown\ |\ \diagup Py \\ Pt \\ CH_3\diagup\ |\ \diagdown Py \\ Py \end{array}\right](ClO_4) \qquad (7)$$

The addition of 3 molar equivalents of ligand (*e.g.* pyridine) caused the ready displacement of the solvent molecules to form the white crystalline tris(ligand)salt [eqn. (7)].

Methyl iodide does not react with $PtR_2(COD)$ [$R = CH_2C_6H_5, CH_2Si(CH_3)_3$]. Iodine, however, reacted with $Pt(CH_2C_6H_5)_2(COD)$ to give a mixture of $[Pt(CH_2C_6H_5)_2I_2]_x$ and $Pt(CH_2C_6H_5)I(COD)$ and with $Pt[CH_2Si(CH_3)_3]_2(COD)$ to give only $Pt[CH_2Si(CH_3)_3]I(COD)$. Two reaction pathways [Shown in eqns. (8) and (9)] are possible for the formation of the PtRI(COD) species.



(8)



(9)

Eqn. (8) involves a concerted bond scission mechanism with elimination of alkyl iodide. Eqn. (9) involves initial oxidation of Pt^{II} to Pt^{IV} to give an intermediate platinum(IV) olefin compound which may then reductively eliminate to give PtRI(COD) or displace 1,5-cyclooctadiene to give Pt^{IV} polymers. Although we have no direct evidence at this time to support either mechanism we favour eqn. (9) since it offers a possible route to the two products obtained from the reaction of $Pt(CH_2C_6H_5)_2(COD)$ with iodine.

TABLE 3

^{19}F AND ^{1}H NMR DATA[a] FOR TRIFLUOROMETHYLPLATINUM COMPLEXES

Complex[b]	$\delta(Pt\text{–}CF_3)$	$^2J(Pt\text{–}CF_3)$	*Other resonances and couplings*
$Pt(CF_3)_2(NC_5H_4CH_3)_2$	24,80	793	$\delta(CH_3)$ 2.66, $\delta(\alpha\text{–}H)$ 8.56, $^3J(PtH)$ 20.4, $\delta(\beta\text{–}H)$ 7.28
$Pt(CF_3)_2[Sb(C_6H_5)_3]_2$	11,09	791	
$Pt(CF_3)_2[(CH_3)_2NCH_2CH_2N(CH_3)_2]$	24,60	752	$\delta(NCH_3)$ 2.81, $^3J(Pt\text{–}H)$ 24.1, $\delta(NCH_2)$ 2.70, $^3J(PtH)$ 15,0
$Pt(CF_3)_2(\pi\text{-}1,5\text{-}C_8H_{12})$	29,73	736	$\delta(CH)$ 5.75, $J(PtH)$ 42, $\delta(CH_2)$ 2,59
$Pt(CF_3)_2$ Bipy	23,90	741	
$Pt(CF_3)_2[As(C_6H_5)_3]_2$	29,01	731	
$Pt(CF_3)_2(CNC_2H_5)_2$	24,20	719	$\delta(CH_3)$ 1.50, $^5J(Pt\text{–}H)$ 2.3, $\delta(CH_2)$ 3.77
$Pt(CF_3)_2[As(CH_3)_3]_2$	19,61	713	$\delta(AsCH_3)$ 1,51, $^3J(Pt\text{–}H)$ 13.0
$Pt(CF_3)_2[P(CH_3)_2(C_6H_5)]_2$	21,60	627	$\delta(PCH_3)$ 1.56, $^3J(PtH)$ 21.0, $^2J(PH)$ 9.6, $^3J(PF)$ 7.2
$Pt(CF_3)_2[P(CH_3)_2(C_6H_5)]_2I_2$	10,41(t)	289	$\delta(PCH_3)$ 2.55, $^3J(Pt\text{–}H)$ 18.7, $^2J(PH)$ 4.0, $^3J(PF)$ 8,4
$Pt(CF_3)_2(CNC_2H_1)_2I_2$	11,61	452	$\delta(CH_3)$ 1.59, $\delta(CH_2)$ 4.15
$Pt(CF_3)_2$ Bipy I_2	10,21	441	
$[Pt(CF_3)_2]_2(DPPA)_2$	[c]		

[a] Spectra were recorded in CH_2Cl_2 or $CHCl_3$ solutions. ^{19}F chemical shifts are in ppm upfield from $CFCl_3$ and ^{1}H chemical shifts are in ppm downfield from $Si(CH_3)_4$; t triplet. [b] Bipy = 2,2′-bipyridine, DPPA = 1,2-bis(diphenylphosphino)acetylene. [c] Complex too insoluble for NMR measurements.

D. Perfluoroalkylplatinum complexes; oxidative addition and displacement reactions

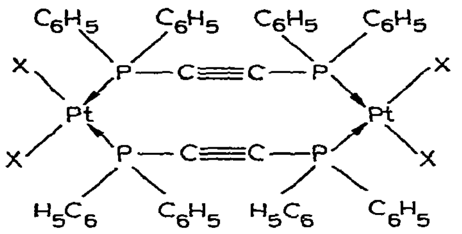
During the past several years organometallic chemists have been interested in synthesizing fluorocarbon transition metal complexes because of the greater stability of these compounds compared to their hydrocarbon analogues. Several methods have been developed[27] for the preparation of such compounds: (1) the reaction of metal carbonyl anions with perfluoroacyl halides followed by decarbonylation; (2) nucleophilic substitution of fluoride with metal carbonyl groups by reactions of fluorinated olefins or aromatic compounds with metal carbonyl anions; (3) addition of fluoroolefins, fluorinated alkynes or perfluoroalkyl iodides to appropriate transition metal systems, particularly those in low oxidation states; (4) reactions of metal halide derivatives with fluoroalkyl or fluoroaryl derivatives of electropositive metals such as lithium or magnesium; (5) reactions of transition metal halide compounds with silver fluorocarbon derivatives[28]. We have now found a very convenient method for the preparation of a variety of bis(perfluoroalkyl)platinum compounds.

In an attempt to prepare $[Pt(CH_3)_2(CF_3)I]_4$ by the oxidative addition of trifluoromethyl iodide to $Pt(CH_3)_2COD$ we found the major product of the reaction to be $Pt(CF_3)_2COD$ with some $[Pt(CH_3)_3I]_4$. There are two possible reaction pathways as in the reaction of iodine with Pt^{II}–COD compounds, *i.e.* (*i*) a concerted mechanism involving scission of the $Pt–CH_3$ bond by CF_3I giving CH_3I and (*ii*) an oxidative addition mechanism involving formation of $Pt(CH_3)_2(CF_3)(COD)I$, elimination of CH_3I to give $Pt(CH_3)(CF_3)(COD)$ and a further oxidative addition-reductive elimination reaction. The latter reaction would be expected to proceed very slowly since $Pt^{II}–CF_3$ complexes are fairly electrophilic and hence oxidized only with strong oxidizing agents such as iodine[8]. The concerted mechanism is favoured although it is possible that this bond scission may involve radicals. The formation of $[Pt(CH_3)_3I]_4$ presumably results from the addition of some of the generated methyl iodide to $Pt(CH_3)_2COD$.

The 1,5-cyclooctadiene in $Pt(CF_3)_2(COD)$ is more labile than in $Pt(CH_3)_2(COD)$ due to (*a*) the high *trans*-influence of the CF_3 group and (*b*) the greater electronegativity of CF_3, which contracts the Pt-5*d* orbitals and synergistically weakens the Pt–COD bond. Therefore a variety of ligands readily displace COD from $Pt(CF_3)_2(COD)$ forming a series of complexes $Pt(CF_3)_2L_2$ [$L = CNC_2H_5$, $P(CH_3)_2(C_6H_5)$, $As(CH_3)_3$, Bipy, $4\text{-}CH_3C_5H_4N$, $Sb(C_6H_5)_3$, $As(C_6H_5)_3$, $(C_6H_5)_2PC\equiv CP(C_6H_5)_2$, and $(CH_3)_2NCH_2CH_2N(CH_3)_2$]. Although many more compounds could readily be obtained, we have only prepared a few with ligands covering a range of *trans*-influence to emphasize the versatility of the reaction. The products are stable crystalline solids, soluble in polar solvents.

The values of $^2J(Pt–CF_3)$ for these complexes (Table 3) are dependent on the platinum hybridization[29], specifically on the amount of Pt-6*s* character in the $Pt–CF_3$ bond. Therefore the ligands L, may be arranged in an order of increasing *trans*-influence as follows: $4\text{-}CH_3C_5H_4N < Sb(C_6H_5)_3 < (CH_3)_2NCH_2CH_2N(CH_3)_2 <$ 1,5-cyclooctadiene $<$ Bipy $< As(C_6H_5)_3 < CNC_2H_5 < As(CH_3)_3 < P(CH_3)_2(C_6H_5)$. The phosphine methyl resonances of $Pt(CF_3)_2[P(CH_3)_2(C_6H_5)]_2$ appear as doublets, flanked by ^{195}Pt satellites, confirming the *cis*-stereochemistry.

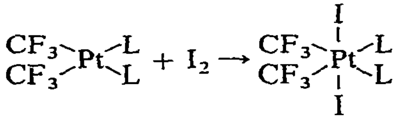
The acetylenic phosphine $(C_6H_5)_2P–C\equiv C–P(C_6H_5)_2$ (DPPA) readily displaces COD from $PtX_2(COD)$ $X = CH_3$, CF_3 to form the binuclear complexes (II).



(II)

Carty and Efraty[30] have prepared a number of transition metal DPPA complexes and have examined the acetylenic C≡C stretching frequency in the solid state Raman spectra. The low value of $\nu(C{\equiv}C)$ in the free ligand was attributed to a lowering of the C≡C bond order resulting from a drift of π-electron density from the carbon p_π-orbitals to phosphorus d_π-orbitals. It was suggested that back-bonding $M(d_\pi) \rightarrow P(d_\pi)$ would decrease the π-electron drift from the carbon $2p_\pi$-orbitals to phosphorus d_π-orbitals, causing $\nu(C{\equiv}C)$ to move to higher frequency. Consequently the more positive $\Delta\nu(C{\equiv}C)$ becomes, the greater is the $M \rightarrow P$ π-bonding. The values of $\Delta\nu(C{\equiv}C)$ for the complexes (II), X = Cl[30], CF_3, CH_3 are 39, 34, 27 cm^{-1} respectively. If the explanation of $P(d_\pi)$–$C(p_\pi)$ bonding is correct, these results infer that there is a greater positive charge on phosphorus for the methylplatinum complex than for the chloro analogue.

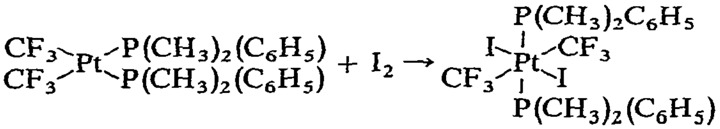
The oxidative addition of iodine to $Pt(CF_3)_2L_2$ [L = CNC_2H_5, Bipy, $P(CH_3)_2(C_6H_5)$] was also studied. For the isocyanide and bipyridyl complexes the iodine gave exclusively the *trans*-addition product. [eqn. (10)].



$$(CF_3)_2Pt(L)_2 + I_2 \rightarrow (CF_3)_2Pt(I)_2(L)_2 \qquad (10)$$

L = CNC_2H_5, Bipy

However, the addition of iodine to $Pt(CF_3)_2[P(CH_3)_2(C_6H_5)]_2$ gave a brown crystalline solid whose ^{19}F NMR showed a triplet pattern with platinum satellites, $^2J(Pt{-}F)$ 289, consistent with *trans*-CF_3 groups[8]. The phosphine methyl resonances appear as "virtually" coupled triplets[31], confirming the stereochemistry shown in eqn. (11).



$$(CF_3)_2Pt[P(CH_3)_2(C_6H_5)]_2 + I_2 \rightarrow I(CF_3)Pt(CF_3)(I)[P(CH_3)_2C_6H_5][P(CH_3)_2(C_6H_5)] \qquad (11)$$

The phosphine complex $Pt(CF_3)_2[P(CH_3)_2(C_6H_5)]_2$ did not react with tetracyanoethylene[32] or hexafluorobutyne, unlike the analogous methylplatinum complex[33,34].

The triphenylstibine complex *cis*-$Pt(CF_3)_2[Sb(C_6H_5)_3]_2$ was not oxidized with iodine.

The reaction between C_2F_5I and *cis*-$Pt(CH_3)_2(COD)$ proceeds smoothly giving mainly $Pt(C_2F_5)_2(COD)$ and some $[Pt(CH_3)_3I]_4$. The perfluoroethyl compound could not be isolated pure, however the cyclooctadiene was displaced by excess triphenylphosphine to give $Pt(C_2F_5)_2[P(C_6H_5)_3]_2$. Similar reactions with perfluoroisopropyl iodide and n-perfluoropropyl iodide and $Pt(CH_3)_2COD$ gave a mixture of products of which none could be isolated in pure form.

CONCLUSIONS

From our present and previous studies of methyl and trifluoromethyl platinum complexes, we can now arrive at several generalizations as follows:

(*i*). Both CH_3 and CF_3 have a high *trans*-influence[29] (*i.e.* defined as a *trans* bond weakening effect)[35].

(*ii*). Both CH_3 and CF_3 contain a large amount of Pt(6*s*) orbital contribution in the Pt–C bond as shown from NMR coupling constants[29].

(*iii*). Pt–CF_3 complexes are much more thermally stable than analogous Pt–CH_3 complexes.

(*iv*). Pt–CF_3 complexes are much less nucleophilic than Pt–CH_3 complexes, as shown by (*a*) oxidative addition reactions; *trans*-$Pt(CH_3)I[P(CH_3)_2(C_6H_5)]_2$ is oxidized by CF_3I to give $Pt(CH_3)(CF_3)I_2[P(CH_3)_2(C_6H_5)]_2$[7] whereas *trans*-$Pt(CF_3)I[P(CH_3)_2(C_6H_5)]_2$ is not oxidized by CH_3I or CF_3I[8]; (*b*) reactions with dilute mineral acids; $Pt(CH_3)_2(COD)$ reacts instantaneously with HCl whereas $Pt(CF_3)_2(COD)$ is stable to HCl; (*c*) reactions with olefins or acetylenes bearing electron withdrawing substituents, *cis*-$Pt(CF_3)_2[P(CH_3)_2(C_6H_5)]_2$ does not react with CF_3–C≡C–CF_3 whereas $Pt(CH_3)_2[P(CH_3)_2C_6H_5]_2$ is very reactive[32]; (*d*) reactions of CH_3–Pt^+ and CF_3–Pt^+ cations with unsaturated organic molecules[29].

(*v*). There appears to be no significant π-back bonding from platinum to either the CF_3 or CH_3 group and the Pt–R bond is very covalent ($R=CF_3$, CH_3)[29].

EXPERIMENTAL

Analytical and physical data for new platinum complexes are given in Tables 4 and 5.

^1H and ^{19}F NMR spectra were recorded on a Varian HA100 spectrometer, the former at 100 MHz and the latter at 94.1 MHz.

Analyses were obtained from Schwarzkopf Microanalytical Laboratories Inc., Woodside, N.Y. and Chemalytics Inc. Tempe, Arizona.

Only representative preparations will be described since many of the complexes were prepared by similar methods. A few of the compounds have been previously prepared, however the following methods gave much better yields. All reactions were performed with "spectro-analyzed" solvents without purification except that the diethylether used in the Grignard or lithium reactions was dried over $LiAlH_4$ and distilled under nitrogen.

(*i*). $Pt(COD)I_2$

To a solution of K_2PtCl_4 (10 g) in 160 ml of distilled water was added 110 ml of n-propanol, 20 ml of 1,5-cyclooctadiene and 0.150 g of $SnCl_2$. The mixture was magnetically stirred for two days (or until the solution was nearly colourless), during

TABLE 4, PHYSICAL AND ANALYTICAL DATA FOR NEW PLATINUM COMPLEXES

Complex[a]	*Analysis found (calcd.) (%)* *C*	*H*	*Colour*	*Melting point*[b] *(°C)*	*Recrystallization solvents*
$Pt(CH_3)_2(CNC_6H_4CH_3)_2$	46.87 (47.05)	4.10 (4.39)	White	82–84	$CH_2Cl_2/n\text{-}C_5H_{12}$
$Pt(CH_3)_2[P(p\text{-}C_6H_4CH_3)_3]_2$	63.33 (63.43)	5.59 (5.81)	White	230–240 (dec)	$CH_2Cl_2/n\text{-}C_5H_{12}$
$[Pt(CH_3)_2]_2(DPPA)_2$	53.93 (54.33)	4.10 (4.23)	White	264–266	$CH_2Cl_2/n\text{-}C_5H_{12}$
$Pt(CH_3)_2(CNC_2H_5)_2$	28.84 (28.66)	4.89 (4.81)	White	39–41	$(C_2H_5)_2O/n\text{-}C_5H_{12}$
$Pt(CH_3)_2[(CH_3)_2NCH_2CH_2N(CH_3)_2]$	28.03 (28.15)	6.21 (6.50)	White	> 143 (dec)	$CH_2Cl_2/(C_2H_5)_2O$
$Pt(C_6H_5)_2(CNC_6H_4CH_3)_2$	57.47 (57.50)	4.07 (4.12)	Yellow	> 130 (dec)	$CH_2Cl_2/n\text{-}C_5H_{12}$
$Pt(CH_3)Cl(COD)$	30.45 (30.55)	4.30 (4.27)	White	166–167	CH_3OH
$Pt(CH_3)Cl(CNC_6H_4CH_3)_2$	42.40 (42.55)	3.59 (3.57)	White	> 120 (dec)	$CH_2Cl_2/n\text{-}C_5H_{12}$
$Pt(C_6H_5)Cl(COD)$	40.66 (40.44)	4.23 (4.12)	White	166–168	$CH_2Cl_2/n\text{-}C_5H_{12}$
$Pt(CH_2C_6H_5)_2(COD)$	54.01 (54.01)	5.23 (5.23)	White	112–115	$CH_2Cl_2/n\text{-}C_5H_{12}$
$Pt(CH_2C_6H_5)Cl(COD)$	41.83 (41.92)	4.36 (4.46)	White	136–138	$CH_3OH/(C_2H_5)_2O$
$Pt(CH_3)Cl$ Bipy	33.61 (33.72)	2.73 (2.83)	Yellow	248–252	$CH_2Cl_2/(C_2H_5)_2O$
$Pt(CH_3)Cl(Phen)$	35.01 (35.18)	2.52 (2.50)	Yellow	310–320	$(CH_3)_2CO/(C_2H_5)_2O$
$[Pt(CH_3)$ Bipy $(NCC_6H_4OCH_3)](PF_6)$	35.25 (35.41)	2.91 (2.81)	Yellow	232–233	$(CH_3)_2CO/(C_2H_5)_2O$
$Pt(C_6H_5)I(COD)$	32.94 (33.15)	3.43 (3.38)	Yellow	125–130	$CH_2Cl_2/(C_2H_5)_2O$
$Pt(CH_3)_2(CNC_2H_5)_2Br_2$	19.09 (19.41)	3.17 (3.26)	Yellow	70–73	$CH_2Cl_2/n\text{-}C_5H_{12}$
$Pt(CH_3)_2(COCH_3)Cl$[c]	16.00 (15.80)	2.92 (2.46)	White	> 130 (dec)	$CH_2Cl_2/n\text{-}C_5H_{12}$
$Pt(CH_3)_2(COCH_3)(4\text{-}CH_3C_5H_4N)_2Cl$	39.78 (40.04)	4.66 (4.83)	White	137–138	$(C_2H_5)_2O/n\text{-}C_5H_{12}$
$Pt(C_2H_5)_2I_2$[d]	9.46 (9.48)	1.68 (1.99)	Brown		
$Pt(C_2H_5)_2(4\text{-}CH_3C_5H_4N)_2I_2$	27.49 (27.72)	3.37 (3.49)	Gold	> 150 (dec)	CH_3OH
$Pt(C_2H_5)_2(CH_3)I$[e]	15.36 (15.20)	3.28 (3.32)	White	> 200 (dec)	$CHCl_3/(CH_3)_2CO$
$Pt(C_2H_5)_2(CH_3)(NC_5H_5)_2I$	32.73 (32.56)	4.20 (4.19)	White	130–132	$CH_3OH/n\text{-}C_5H_{12}$
$[Pt(C_2H_5)_2(CH_3)(NC_5H_5)_3](ClO_4)$	39.80 (39.71)	4.67 (4.66)	White	143–145	$CH_3OH/(C_2H_5)_2O$
$Pt(CH_2C_6H_5)I(COD)$	34.47 (34.60)	3.63 (3.65)	Yellow	> 120 (dec)	$(C_2H_5)_2O/n\text{-}C_5H_{12}$
$Pt(CH_2C_6H_5)_2I_2$[f]	26.31 (26.64)	2.04 (2.24)	Brown		
$Pt[CH_2Si(CH_3)_3](COD)I$	27.97 (27.86)	4.29 (4.48)	White	51–53	CH_3OH

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[a] DPPA = 1,2-bis(diphenylphosphino)acetylene, COD = 1,5-cyclooctadiene, Bipy = 2,2′-bipyridine, Phen = 1,10-phenanthroline. [b] Melting points are uncorrected. [c] Found: Cl, 12.06. Calcd.: 11.68%. [d] Found: I, 49.83. Calcd.: 50.06%. [e] Found: I, 32.01. Calcd.: 32.12%. [f] Found: I, 39.84. Calcd.: 40.20%.

TABLE 5

ANALYTICAL AND PHYSICAL DATA FOR PERFLUOROALKYLPLATINUM COMPLEXES

Complex[a]	*Colour*	*Analyses found (calcd.) (%)*			*Melting point*[b] (°C)	*Recrystallization*[c] *solvents*
		C	*H*	*F*		
$Pt(CF_3)_2[(CH_3)_2NCH_2CH_2N(CH_3)_2]$	White	21.33	3.68	25.44	>200 (dec)	CH_2Cl_2/n-C_5H_{12}
		(21.38)	(3.59)	(25.40)		
$Pt(CF_3)_2(NC_5H_4CH_3)_2$	White	32.26	2.59	21.64	250–252	CH_2Cl_2/n-C_5H_{12}
		(32.38)	(2.72)	(21.95)		
$Pt(CF_3)_2[Sb(C_6H_5)_3]_2$	White	44.18	3.17	10.95	150–151	$(CH_3)_2CO$/n-C_5H_{12}
		(43.92)	(2.91)	(10.97)		
$Pt(CF_3)_2(\pi$-1,5-$C_8H_{12})$	White	27.11	2.70	27.27	179–181	CH_2Cl_2/n-C_5H_{12}
		(27.22)	(2.74)	(27.06)		
$Pt(CF_3)_2$Bipy	Yellow	29.17	1.54	23.26	303–305	DMF/$(C_2H_5)_2O$
		(29.46)	(1.65)	(23.30)		
$Pt(CF_3)_2[As(C_6H_5)_3]_2$	White	48.09	3.46	11.67	245–250	$CH_2Cl_2/(C_2H_5)_2O$
		(48.27)	(3.20)	(12.06)		
$Pt(CF_3)_2(CNC_2H_5)_2$	White	17.24	1.74	20.38	130–132	CH_2Cl_2/n-C_5H_{12}
		(17.37)	(1.82)	(20.61)		
$Pt(CF_3)_2[P(CH_3)_2(C_6H_5)]_2$	White	35.56	3.68	18.88	188–190	$CH_2Cl_2/(C_2H_5)_2O$
		(35.47)	(3.64)	(18.71)		
$Pt(CF_3)_2[P(CH_3)_2(C_6H_5)]_2I_2$	Brown	24.85	2.46	12.91	128–130	CH_2Cl_2/n-C_5H_{12}
		(25.04)	(2.57)	(13.21)		
$Pt(CF_3)_2(CNC_2H_5)_2I_2$	Brown	12.01	1.21	14.21	145–150	CH_2Cl_2/n-C_5H_{12}
		(11.91)	(1.25)	(14.13)		
$Pt(CF_3)_2Bipy_2I_2$	Red	19.28	1.12	15.13	>105 (dec)	DMF/$C_2H_5)_2O$
		(19.40)	(1.08)	(15.36)		
$[Pt(CF_3)]_2(DPPA)_2$	White	46.47	2.93	15.53	274–276	$(CH_3)_2CO/(C_2H_5)_2O$
		(46.25)	(2.77)	(15.69)		
$Pt(C_2F_5)_2[P(C_6H_5)_3]_2$	White	50.25	3.55	19.14	235–237	$CH_2Cl_2/(C_2H_5)_2O$
		(50.16)	(3.16)	(19.84)		

[a] Bipy = 2,2′-bipyridine, DPPA = 1,2-bis(diphenylphosphino)acetylene. [b] Melting points are uncorrected. [c] DMF = dimethylformamide.

which time a white precipitate formed. The mixture was filtered, washed with distilled water (100 ml) and 20 ml of ethanol, then air-dried. The yield of $PtCl_2$(COD) was usually better than 8.8 g (98 %). The dichloride was readily converted to the diiodide in 98 % yield by the addition of a slight excess of NaI [7 g NaI for 8.2 g $PtCl_2$(COD)] to a suspension of $PtCl_2$(COD) in acetone. The solution immediately turned yellow and the acetone was removed by rotary evaporation. The residue was collected on a frit and washed three times with 50 ml portions of distilled water and air-dried.

(ii). $Pt(CH_3)_2(COD)$

To an ice-cold solution of PtI_2(COD) (11.8 g) in 100 ml of diethylether, under nitrogen was added a slight excess of methyllithium (30 ml of a 1.95 *M* solution in ether). The solution was stirred for two hours and hydrolyzed at 0° with an ice-cold saturated aqueous solution of ammonium chloride. The ether layer was separated and the aqueous layer extracted with three 50 ml portions of diethyl ether. The ether fractions were dried over anhydrous magnesium sulphate containing a small amount of activated charcoal. The solution was filtered and the ether removed by rotary evaporation to give white crystals of $Pt(CH_3)_2$(COD) (6.05 g, 87 %).

(iii). $Pt(C_2H_5)_2(COD)$

An ethylmagnesium iodide solution was prepared from 1.0 g of Mg and 6.24 g of ethyl iodide (3.2 ml) in 100 ml of dried ether. This solution was filtered under nitrogen and cooled to 0°, then $PtI_2(COD)$ (5.0 g) was added. The solution was stirred at 0° for three hours, hydrolyzed and dried as in *(ii)*. The ether was removed to give a pale yellow oil, which solidified on cooling to 0°. The yield of $Pt(C_2H_5)_2(COD)$ (m.p. 25–30°) was 79% (2.55 g).

(iv). $Pt(CH_2C_6H_5)_2(COD)$

A solution of the benzyl Grignard, prepared from magnesium (1.0 g) and 6.84 g $C_6H_5CH_2Br$ in 100 ml of dried ether, was filtered and $PtI_2(COD)$ (5.0 g) was added. The solution was stirred for 4 h at room temperature and worked up as in *(ii)*. The yield was 3.55 g (82%).

(v). $[Pt(CH_3)_2I_2]_x$

To a solution of $Pt(CH_3)_2(COD)$ (0.682 g) in 50 ml of dichloromethane was added a solution of iodine (0.52 g) in dichloromethane. There was an immediate orange-red precipitate; the solution was stirred for 1 h, filtered and washed with ether and pentane. Yield 0.875 g (91%). The dibromide was prepared similarly using bromine.

(vi). $Pt(CH_3)_2(CNC_2H_5)_2Br_2$

To a suspension of $[Pt(CH_3)_2Br_2]_x$ (0.150 g) in 8 ml of dichloromethane was added 0.055 ml of ethylisocyanide. The mixture was stirred for 20 h to give a clear yellow solution which was passed through a 1" Florisil column, eluting with dichloromethane. The volume was reduced and the addition of pentane caused the formation of yellow needle-shaped crystals. Yield 0.139 g (68%).

(vii). $Pt(CH_3)(C_2H_5)_2I$

$Pt(C_2H_5)_2(COD)$ (0.402 g) was dissolved in 5 ml of iodomethane. After 2 h large block crystals formed. After 10 h the iodomethane was removed by rotary evaporation. The white solid was dissolved in chloroform and acetone was added to give white needles. The solution was cooled for several hours, filtered and the crystals were washed with pentane. The yield was 0.360 g (82%).

(viii). $[Pt(CH_3)(C_2H_5)_2(NC_5H_5)_3](ClO_4)$.

To a solution of $Pt(CH_3)(C_2H_5)_2I$ (0.158 g) and pyridine (0.100 ml) in 5 ml of dichloromethane was added a solution of $AgClO_4$ (0.084 g) in 5 ml of acetone. Silver iodide precipitated immediately and after the mixture had been stirred for 10 min, the precipitate was removed by centrifugation. The solvent was removed by rotary evaporation to give a clear colourless oil, which was dissolved in 2 ml of methanol. Ether was added and the solution was cooled to 0°. Scratching the flask initiated the crystallization of white needles which were filtered and washed with ether. Yield 0.178 g (74%).

(ix). $Pt(CH_3)_2(COCH_3)Cl$

$Pt(CH_3)_2(COD)$ (0.844 g) was dissolved in the minimum amount of diethylether and a molar equivalent of acetyl chloride (0.20 ml) was added. After 12 h white crystals had deposited; the solution was cooled at 0° for several hours and the ether was decanted. Yield 0.650 g (84%).

(*x*). $Pt(CH_3)_2(COCH_3)(4\text{-}CH_3C_5H_4N)_2Cl$

$Pt(CH_3)_2(COCH_3)Cl$ (0.070 g) was dissolved in 2 ml of chloroform and 4-methylpyridine (0.043 g) was added and the solution became warm. The solvent was removed to give a clear oil that was crystallized from ether and pentane. Yield 0.084 g (75%).

(*xi*). *Reaction of* $Pt(CH_2C_6H_5)_2(COD)$ *with iodine*

To a solution of $Pt(CH_2C_6H_5)_2(COD)$ (0.680 g) in ether was added a solution of iodine (0.366 g) in ether. The solution became red and over a period of 1 h a brown powder precipitated. It was filtered and identified as $Pt(CH_2C_6H_5)_2I_2$ [yield 48% based on $Pt(CH_2C_6H_5)_2(COD)$]. The yellow filtrate was reduced in volume and pentane was added; after cooling yellow needles of $Pt(CH_2C_6H_5)I(COD)$ separated (45% yield). They were filtered, washed with pentane and air-dried.

(*xii*). $[Pt(C_2H_5)_2I_2]_x$

To an ice-cold solution of $Pt(C_2H_5)_2(COD)$ (0.412 g) in ether was added a molar equivalent of iodine (0.290 g) in ether. A brown powder separated immediately and after being stirred for 10 min the solution was filtered and the brown powder was washed with ether and pentane. Yield 0.380 g (75%).

(*xiii*). $Pt(C_2H_5)_2(4\text{-}CH_3C_5H_4N)_2I_2$

$Pt(C_2H_5)_2I_2$ (0.138 g) was suspended in benzene and 2 molar equivalents of 4-methylpyridine (0.050 g) were added. After 1 h a yellow solution resulted; the benzene was removed by rotary evaporation to give golden crystals which were dissolved in warm methanol. The solution was cooled and golden yellow needles separated, 0.085 g (46%). The crystals were filtered and washed with pentane.

(*xiv*). $Pt(CH_3)_2(p\text{-}CNC_6H_4CH_3)_2$

$Pt(CH_3)_2(COD)$ (0.252 g) was dissolved in 5 ml of acetone and *p*-tolylisocyanide (0.177 g) was added. The solution was stirred for 3 h and the solvent removed by rotary evaporation to give dirty yellow crystals which were washed with pentane to remove cyclooctadiene and free isocyanide. The crystals were dissolved in 2 ml of dichloromethane and passed through a 1" Florisil column, eluting with CH_2Cl_2. The volume was reduced and the addition of pentane induced crystallization. The flask was cooled for 2 h and the white crystals were filtered and washed with pentane. Yield 0.267 g (77%).

(*xv*). $Pt(CH_3)_2[(CH_3)_2NCH_2CH_2N(CH_3)_2]$

$Pt(CH_3)_2(COD)$ (0.40 g) was dissolved in 2 ml of *N,N,N',N'*-tetramethylethylenediamine and the solution was heated to 100° for 1 h. The excess amine was removed under vacuum to give an oil which was taken up in dichloromethane. The addition of diethyl ether, and subsequent cooling gave white crystals which were filtered and washed with ether. Yield 0.375 g (91%).

(*xvi*). $Pt(CF_3)_2(COD)$

$Pt(CH_3)_2(COD)$ (2.80 g) was placed in a 10 ml thick-walled Carius tube and dissolved in 3 ml of dichloromethane. The solution was frozen and degassed twice using conventional freeze-thaw vacuum techniques. Trifluoromethyl iodide (20 mmoles, slightly greater than a 2 molar equivalent) was condensed into the tube and the Carius tube was sealed. The solution was allowed to warm up to ambient temperature and was shaken for 4 days during which time several large crystals deposited from solution. The tube was then opened, the solution filtered to give 0.40 g of $Pt(CH_3)_3I$. The filtrate was passed through a short Florisil column, eluting with dichloromethane, to give a pale yellow solution. The volume was reduced and pentane added to give white crystals. After cooling for 2 h the crystals were filtered and washed with pentane. Yield 2.25 g (61 %).

(*xvii*). $Pt(CF_3)_2[P(CH_3)_2(C_6H_5)]_2$

To a solution of $Pt(CF_3)_2(COD)$ (0.381 g) in 5 ml of dichloromethane was added $P(CH_3)_2(C_6H_5)$ (0.238 g). The solution was stirred for 2 h and the solvent was removed by rotary evaporation to give a white solid that was recrystallized from dichloromethane and pentane. Yield 0.480 g (92 %).

(*xviii*). $Pt(CF_3)_2$ *Bipy*

2,2'-Bipyridine (0.083 g) was added to an acetone solution of $Pt(CF_3)_2(COD)$ (0.234 g). The solution turned yellow and after 15 min the solvent was removed to give a yellow solid. Recrystallization from dimethylformamide and ether yielded 0.200 g (77 %).

(*xix*). $Pt(CF_3)_2[P(CH_3)_2(C_6H_5)]_2I_2$

Iodine (0.024 g) was added to a solution of $Pt(CF_3)_2[P(CH_3)_2(C_6H_5)]_2$ in dichloromethane (1 ml). There was an immediate colour change and the addition of pentane gave brown needles. Yield 0.066 g (82 %).

(*xx*). $Pt(CH_3)Cl(COD)$

$Pt(CH_3)_2(COD)$ (2.84 g) was dissolved in 30 ml of dichloromethane and 20 ml of methanol. Acetyl chloride (0.58 g, 0.61 ml) was added dropwise and effervescence was immediately observed. The solution was stirred for 10 min after all of the acetyl chloride had been added and the volume of the solution was reduced to about 5 ml giving white crystals. After cooling for 2 h the solution was filtered and the crystals were washed with pentane. Yield 2.70 g (97 %).

(*xxi*). $Pt(CH_3)Cl(p\text{-}CNC_6H_4CH_3)_2$

Acetyl chloride (0.036 ml) was added to a solution of $Pt(CH_3)_2(CNC_6H_4CH_3)_2$ (0.235 g) in 2 ml of dichloromethane and 2 ml of methanol. After effervescence had ceased, the volume of the solution was reduced and ether was added to give white crystals. After cooling at 0° the solution was filtered and the crystals were washed with pentane. Yield 0.214 g (88 %).

(*xxii*). $Pt(CH_3)Cl$ *Bipy*

$Pt(CH_3)Cl(COD)$ (0.215 g) was dissolved in 5 ml of dichloromethane and bipyridine (0.061 g) was added. The solution was refluxed for 30 min and cooled to give yellow needles. Ether was added and the solution was cooled for several hours at 0° and filtered. Yield 0.240 g (98 %).

(xxiii). $[Pt(CH_3)\,Bipy\,(NCC_6H_4OCH_3)](PF_6)$

$AgPF_6$ (0.120 g) in 2 ml of acetone was added to a solution of $Pt(CH_3)ClBipy$ (0.185 g) and *p*-methoxybenzonitrile (0.063 g) in 5 ml of acetone. AgCl slowly precipitated and after 1 h was removed by centrifugation to give a pale yellow solution. The volume was reduced and ether was added to give pale yellow needles. After cooling at 0° for 2 h the crystals were filtered and washed with ether. Yield 0.160 g (53 %). Yield was 80 %.

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