found to form insoluble, polymeric species upon heating and concentration. Second, blue compounds with different average platinum oxidation states can be obtained by varying the mole ratio of the starting materials. Third, the mixed-valence absorption profiles at various temperatures are examined with use of Hush's model. Our optical and magnetic results strongly suggest that the platinum phthalimide blues are best described as class II–class III borderline mixed-valence compounds in which there is extensive delocalization but inequivalent metal sites.

Acknowledgment. The authors thank Michel P. Laurent for many helpful discussions. The work described in this paper has been supported by the American Cancer Society.

Registry No. *cis*-$PtI_2(NH_3)_2$, 15978-93-5; potassium phthalimide, 1074-82-4; *cis*-DDP, 15663-27-1.

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Reactivity of Platinum Diolefin Complexes. Roles of Trans Influence and Chelate Effect

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Received August 19, 1980

The complex $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene) reacts with CO and tertiary phosphine to produce *cis*-$[PtCl_2(CO)L]$ (L = PEt_3, P-*n*-Bu_3, $PMePh_2$, PPh_3, $P(C_6H_4F\text{-}p)_3$, or P(c-Hx)$_3$), which have been characterized by infrared and ^{31}P NMR measurements. The reaction was studied by ^{13}C and ^{31}P NMR, infrared and electronic spectroscopies, and possible mechanisms are discussed in terms of the chelate effect of the diolefin. Complexes $[PtR_2(cod)]$ (R = Me or Ph) react with CO to give $[PtR_2(CO)_2]$, while [PtClR(cod)] complexes undergo carbonyl insertion to yield [PtCl(COR)(cod)]. Reactions of these species with $PMePh_2$ were also studied. The ^{13}C NMR spectra and reactions of the cyclooctadiene complexes are discussed in terms of the trans influence of the organo ligands and the chelate effect.

Introduction

Transition-metal complexes of weak donor ligands, and in particular platinum and palladium complexes of the type $[MX_2L_2]$ (M = Pd or Pt, X = anionic ligand, L = weak donor ligand), are useful starting materials in organometallic and coordination chemistry. Their usefulness lies in the ease with which the donor ligand may be displaced. While commonly encountered leaving groups include nitriles,[1-3] dialkyl sulfides,[4] and dialkyl sulfoxides,[5,6] chelating diolefins such as norbornadiene, 1,5-cyclooctadiene, and cyclooctatetraene are especially suitable since they maintain a cis configuration about the metal, and their complexes are stable under the conditions required to modify the other groups around the metal center.[7-9] Subsequent displacement of the diolefin to give the desired product is then a very facile process.

An unusual example of such displacement has been noted[10] in the reaction of $[PtCl_2(nbd)]$ (nbd = norbornadiene) with two different incoming nucleophiles, namely, CO and P(c-Hx)$_3$ or P(*o*-tolyl)$_3$ to give *cis*-$[PtCl_2(CO)(PR_3)]$ complexes. This is particularly convenient since the usual route to *cis*-$[PtCl_2(CO)(PR_3)]$ complexes via cleavage by CO of the chloride-bridged complex $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ is not available with these bulky phosphines.

It was therefore decided to extend this reaction to the 1,5-cyclooctadiene complex, $[PtCl_2(cod)]$, to investigate the mechanism of formation of *cis*-$[PtCl_2(CO)L]$ (where L is tertiary phosphine), and to discover whether this type of reaction could be extended to the [PtClR(cod)] and $[PtR_2(cod)]$ (R = Me or Ph) systems.

Experimental Section

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 60.0, 15.1, and 24.3 MHz, respectively, on a Brüker WP-60 spectrometer operating in the FT mode. Spectra were run for $CDCl_3$ solutions at 25 °C (except where stated); ^1H and ^{13}C chemical shifts were measured relative to Me_4Si, and ^{31}P chemical shifts were measured relative to external H_3PO_4, downfield shifts being positive.

Infrared spectra were measured in $CHCl_3$ solution with use of NaCl solution cells of path length 0.1 mm or as Nujol mulls between CsI plates and were recorded on a Perkin-Elmer 180 spectrophotometer.

Electronic spectra were obtained with the use of a Cary 118 spectrophotometer. Measurements were performed upon $CHCl_3$ solutions in 2-cm quartz cells.

Molecular weight determinations were carried out on $CHCl_3$ solutions at 37 °C with the use of a Perkin-Elmer 115 instrument.

Carbon-13 labeled carbonyl complexes were prepared with use of 90% enriched ^{13}CO obtained from Prochem. The complexes $[PtMe_2(cod)]$, [PtClMe(cod)], $[PtPh_2(cod)]$, and [PtClPh(cod)] were prepared by reported methods.[8] The complexes *cis*-$[PtCl_2(CO)(PR_3)]$ were all prepared similarly, so a typical example only is given.

Preparation of *cis*-$[PtCl_2(CO)(PMePh_2)]$. Carbon monoxide was passed through a suspension of $[PtCl_2(cod)]$ (0.226 g, 0.604 mmol) in chloroform (30 mL). After 1 h, a chloroform solution of $PMePh_2$ (0.121 g, 0.604 mmol) was added dropwise over 30 min, and CO passage was continued for a further 30 min. Concentration of the solution and ether addition caused precipitation of white crystals (0.233 g, 78%).

Preparation of [PtCl(COPh)(cod)]. Carbon monoxide was passed through a solution of [PtClPh(cod)] (0.395 g, 0.951 mmol) in chloroform (20 mL) for 1 h. The volume of the pale yellow solution was reduced, and the addition of ether caused precipitation of pale

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Table I. ^{31}P NMR and Infrared^a Spectral Data for the Complexes *cis*-$[PtCl_2(CO)L]$

L	δ(P), ppm^b	^1J(Pt-P), Hz	ν(CO), cm^{-1}	ν(Pt-Cl), cm^{-1}
PEt_3	21.9	2797	2093	298,343
P-*n*-Bu_3	14.1	2778	2090	297,343
$PMePh_2$	−0.2	2946	2092	298,344
PPh_3	9.5	3057	2108	312,357
$P(C_6H_4F\text{-}p)_3$	6.9	3083	2094	309,348
P(c-Hx)$_3$	36.5	2852	2072	295,339

^{a} Infrared spectra were recorded as Nujol mulls. ^{b} All spectra were recorded for $CDCl_3$ solutions except where L = $P(C_6H_4F\text{-}p)_3$, which was measured in a $CH_2Cl_2/CDCl_3$ solvent mixture.

yellow crystals (0.228 g, 54%), ν(CO) 1638 cm^{-1} (Nujol mull).

Results

When carbon monoxide was passed through a chloroform solution of $[PtCl_2(cod)]$, a pink coloration was seen to develop. Solution infrared studies showed no absorption indicative of a carbonyl group, and the ^{13}C NMR spectrum of a sample stirred under a ^{13}CO atmosphere for 10 days showed only the presence of $[PtCl_2(cod)]$.

The electronic spectrum of such a pink solution, however, exhibited a band at 508 nm, albeit of low extinction coefficient, suggesting the existence of a small amount of a species formed by interaction with carbon monoxide.

Despite the lack of evidence for a carbonyl complex in the ^{13}C NMR spectrum, the addition of $PMePh_2$ to a solution of $[PtCl_2(cod)]$ which had been saturated with carbon monoxide resulted in the formation of *cis*-$[PtCl_2(^{13}CO)(PMePh_2)]$ (δ(C) 156.7, ^2J(P–C) = 6.8 Hz).[11] Treatment of $[PtCl_2(cod)]$ with $AgBF_4$ in the presence of ^{13}CO resulted in some decomposition, and, after filtration, the ^{13}C NMR spectrum showed the presence of some unreacted $[PtCl_2(cod)]$ only (δ(C) 30.9 and 100.0).

The addition of any one of a variety of tertiary phosphines to a chloroform suspension of $[PtCl_2(cod)]$, which had been previously saturated with carbon monoxide, allowed isolation of the corresponding complex *cis*-$[PtCl_2(CO)L]$ (L = PEt_3, P-*n*-Bu_3, $PMePh_2$, PPh_3, $P(C_6H_4F\text{-}p)_3$ or P(c-Hx)$_3$) in good yield. The ^{31}P NMR and infrared spectral data are given in Table I. Previously the complex *cis*-$[PtCl_2(CO)(P(o\text{-tolyl})_3)]$ had been prepared from the norbornadiene complex,[10] but it was found that no reaction of this tertiary phosphine occurred with $[PtCl_2(cod)]$, even in refluxing chloroform.

Addition of $PMePh_2$ to a solution of $[PtCl_2(cod)]$ produced *cis*-$[PtCl_2(PMePh_2)_2]$ (δ(P) −1.2, ^1J(Pt–P) = 3621 Hz) as the only phosphorus-containing product, while tertiary phosphine addition in the presence of $AgBF_4$ gave $[PtCl(PMePh_2)_3]^+$ (δ(P) 9.9 (doublet), ^2J(P–P) = 20 Hz and ^1J(Pt–P) = 2405 Hz, and δ(P) −4.5 (triplet), ^1J(Pt–P) 3591 Hz) as the main product; any $[PtCl(cod)(PMePh_2)]^+$ formed must only have been present as an almost negligible amount.

Reactions of the complexes $[PtR_2(cod)]$ (R = Me or Ph) with carbon monoxide gave infrared and ^{13}C NMR spectra consistent with the complexes $[PtR_2(CO)_2]$ (Tables II and III). Two ν(CO) bands were observed in the solution infrared spectrum in each case, and the high δ(C) and low ^1J(Pt–C) values are typical of CO trans to a ligand of high trans influence.[11] Free 1,5-cyclooctadiene was also detected in the ^{13}C NMR spectrum (δ(C) 28.3 and 128.9). When the complex $[PtPh_2(CO)_2]$ was further treated with $PMePh_2$, displacement of CO occurred to produce *cis*-$[PtPh_2(PMePh_2)_2]$ (δ(P) 0.9, ^1J(Pt–P) = 1760 Hz), which was also obtained by direct interaction of $PMePh_2$ with $[PtPh_2(cod)]$.

Table II. Solution Infrared Data for the Complexes Produced in the Reactions of $[PtR_2(cod)]$ and $[PtClR(cod)]$ with Carbon Monoxide

	ν(CO), cm^{-1}	
	terminal	acyl
$[PtPh_2(CO)_2]$	2125, 2085	
$[PtMe_2(CO)_2]$	2114, 2064	
$[PtCl(COPh)(cod)]$		1640
$[PtClMe(cod)]$ + CO	2145, 2095	1662 (weak)

The unsymmetrical complex $[PtClPh(cod)]$ was found to react readily with carbon monoxide, and with ^{13}CO it produced a ^{13}C NMR spectrum entirely consistent with the aroyl complex $[PtCl(COPh)(cod)]$ (Table III). The large downfield shift and the coupling constant are similar in magnitude to those previously observed for aroylplatinum(II) complexes,[11] and the platinum–carbon couplings indicate that the cyclooctadiene remains coordinated. For the phenyl carbon atoms, couplings to platinum are unresolved, but are clearly much smaller than in $[PtClPh(cod)]$, which is consistent with insertion of a molecule into the carbon–platinum bond. The solution infrared spectrum exhibited a strong aroyl band at 1640 cm^{-1}. Addition of 2 mol equiv of $PMePh_2$ to such a solution gave *trans*-$[PtCl(COPh)(PMePh_2)_2]$ (δ(C) 212.8, ^1J(Pt–C) = 1006 Hz, ^2J(P–C) = 5.9 Hz).[11]

In an attempt to identify the intermediates in the formation of $[PtCl(COPh)(cod)]$, the phenyl complex was treated with ^{13}CO at −60 °C. The ^{13}C NMR spectrum at this temperature showed the presence of some aroyl complex, along with two ^{13}CO resonances at δ(C) 173.6 and 156.8, consistent with CO trans to Ph and Cl, respectively.[11] Warming to room temperature resulted in the disappearance of the carbonyl resonances and total conversion to $[PtCl(COPh)(cod)]$.

Halide abstraction from $[PtCl(COPh)(cod)]$ by $AgBF_4$, and from $[PtClPh(cod)]$ in the presence of CO by $AgBF_4$ or $TlNO_3$, led to extensive decomposition, and ^{13}C NMR and infrared studies of the resulting solutions revealed no identifiable species.

The reaction of $[PtClMe(cod)]$ with CO was also studied by ^1H NMR, ^{13}C NMR, and infrared spectroscopies and proved to be much slower than that of the phenyl complex. The ^{13}C NMR spectrum of a solution which had been treated with ^{13}CO exhibited an acyl resonance at δ(C) 209.3 (^1J(Pt–C) = 886 Hz) and a carbonyl signal at δ(C) 179.9. The ^{13}C signals associated with the cyclooctadiene ligand indicated that little reaction had taken place, and the ^1H NMR spectrum was unchanged except for the presence of a relatively weak methyl proton resonance at δ 1.38 (Table IV). The solution infrared spectrum contained two ν(CO) bands at 2145 and 2095 cm^{-1}, as well as an acyl band at 1662 cm^{-1} (Table III). The slow reaction of the methyl complex relative to its phenyl analogue is not without precedent,[12,13] and the small amounts involved rendered identification of the carbonyl species unpracticable. Treatment of $[PtClMe(cod)]$ with a catalytic amount of $AgBF_4$ in the presence of carbon monoxide produced no change in the solution infrared spectrum compared with that for the "uncatalyzed" reaction.

A number of tertiary phosphine addition reactions were performed on the complexes $[PtClPh(cod)]$ and $[PtCl(COPh)(cod)]$. Addition of 1 mol equiv of $PMePh_2$ to a solution of $[PtClPh(cod)]$ produced *trans*-$[PtClPh(PMePh_2)_2]$ (δ(P) 8.4, ^1J(Pt–P) = 3010 Hz) as the only significant phosphorus-containing species, and introduction of a second mol equiv merely completed this reaction.

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Table III. ^{13}C NMR and Molecular Weight Measurements for the (Cyclooctadiene)platinum Complexes and Their Derivatives Formed by Reaction with Carbon Monoxide

complex	mol wt found	mol wt calcd	δ-(CH)^a	^1J-(Pt–C)^b	δ-(CH$_2$)^a	^2J-(Pt–C)^b	δ-(CO)^a	^1J-(Pt–C)^b	other ^{13}C resonances^c
PtCl$_2$(cod)			100.0	154	31.0				
PtPh$_2$(cod)	465	457	104.5	47	29.9				δ(C) 127.6, ^2J(Pt–C) = 77 Hz; δ(C) 134.7, ^3J(Pt–C) = 35 Hz; δ(C) 122.9, ^4J(Pt–C) = 12 Hz
PtClPh(cod)	409	416	115.8^d	28	32.3	26			δ(C) 128.5, ^2J(Pt–C) = 50 Hz; δ(C) 133.9, ^3J(Pt–C) = 12 Hz; δ(C) 124.5, ^4J(Pt–C) = 8 Hz
			87.2^e	210	28.0	24			
PtMe$_2$(cod)	347	333	99.1	54	30.0				δ(CH$_3$) 4.6, ^1J(Pt–C) not observed
PtClMe(cod)	350	354	113.5^d	31	31.9	24			δ(CH$_3$) 5.3, ^1J(Pt–C) not observed
			83.6^e	216	28.2	23			
PtPh$_2$(CO)$_2$							175.8	881	δ(C) 128.2, ^2J(Pt–C) = 69 Hz; δ(C) 137.4, ^3J(Pt–C) = 43 Hz; δ(C) 125.2, ^4J(Pt–C) = 11 Hz
PtMe$_2$(CO)$_2$							178.0	898	δ(CH$_3$) 17.7, ^1J(Pt–C) not observed
PtCl(COPh)(cod)	446	444	119.9^d	12	31.8	31	207.6	921	aromatic resonances at δ(C) 130.4, 128.4 and 132.4
			86.1^e	232	27.4	30			
PtCl(COMe)(cod)			*f*		*f*		209.3	886	methyl resonance not observed

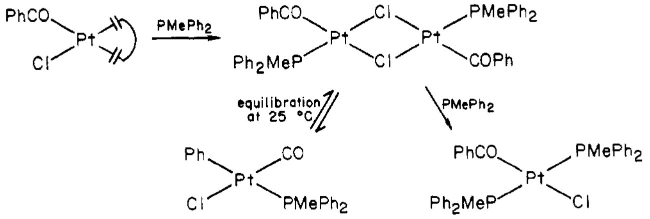
^{a} Chemical shifts are measured downfield of Me$_4$Si. ^{b} Coupling constants are in Hz. ^{c} In the phenyl complexes no resonance was observed for the metallated carbon, perhaps due to the absence of any Nuclear Overhauser Effect. ^{d} Cis to Cl. ^{e} Trans to Cl. ^{f} Insufficient reaction to allow observation of the cyclooctadiene resonances.

Table IV. ^{1}H NMR Data^a for the Complexes [PtMe$_2$(cod)] and [PtClMe(cod)] and the Products of Their Reactions with Carbon Monoxide

complex	δ-(C*H*$_3$)	^2J-(Pt–H), Hz	δ-(C*H*)	^2J-(Pt–H), Hz	δ-(C*H*$_2$)
PtMe$_2$(cod)	0.75	81	4.90	40	2.36
PtClMe(cod)	0.90	71	5.54, 4.64	35, 76	2.40
PtMe$_2$(CO)$_2$	0.89	78			
PtCl(COMe)-(cod)	1.38	48	*b*		*b*

^{a} Spectra were recorded at −40 °C. ^{b} Not observed.

The reaction of 1 mol equiv of PMePh$_2$ with [PtCl(^{13}COPh)(cod)] produced small amounts of the equilibrating[14] complexes [PtClPh(CO)(PMePh$_2$)] (δ(C) 162.2, ^2J(P–C) = 6.8 Hz) and [Pt$_2$(μ-Cl)$_2$(COPh)$_2$(PMePh$_2$)$_2$] (δ(C) 196.6, ^2J(P–C) unresolved)[11] in addition to *trans*-[PtCl(COPh)(PMePh$_2$)$_2$]. Addition of further PMePh$_2$ resulted in complete conversion to *trans*-[PtCl(COPh)(PMePh$_2$)$_2$]. When this reaction was carried out at −60 °C, and monitored by ^{31}P NMR spectroscopy, it was found that some [Pt$_2$(μ-Cl)$_2$(COPh)$_2$(PMePh$_2$)$_2$] (δ(P) −2.8, ^1J(Pt–P) = 5215 Hz[14]), but not [PtClPh(CO)(PMePh$_2$)], was formed with 1 mol equiv of PMePh$_2$, indicating that the dimeric aroyl complex was formed from [PtCl(COPh)(cod)] and PMePh$_2$, while [PtClPh(CO)(PMePh$_2$)] was only formed at ambient temperature by equilibration of the chloride-bridged aroyl complex.



When *trans*-[PtClPh(PMePh$_2$)$_2$] was treated with AgBF$_4$ in the presence of PMePh$_2$, the cationic complex [PtPh(PMePh$_2$)$_3$]$^+$ (δ(P) 2.8 (doublet), ^2J(P–P) = 20 Hz, ^1J(Pt–P) = 2798 Hz and δ(P) −4.0 (triplet), ^1J(Pt–P) = 1792 Hz) was formed. Interestingly, analogous treatment of *trans*-[PtCl(COPh)(PMePh$_2$)$_2$] produced the above species in addition to the [Pt(COPh)(PMePh$_2$)$_3$]$^+$ cation (δ(P) −4.3 (doublet), ^2J(P–P) = 26 Hz, ^1J(Pt–P) = 3015 Hz and δ(P) −8.7 (triplet), ^1J(Pt–P) = 1475 Hz). When *trans*-[PtCl(COPh)(PMePh$_2$)$_2$] was treated with AgClO$_4$ in acetone an intermediate species was detected (δ(P) 8.0, ^1J(Pt–P) = 3286 Hz), presumably the [Pt(COPh)(PMePh$_2$)$_2$(acetone)]$^+$ cation, and PMePh$_2$ addition produced [Pt(COPh)(PMePh$_2$)$_3$]$^+$ only. This suggests that in a noncoordinating solvent rapid rearrangement occurs to fill the vacant coordination site, and the tertiary phosphine then displaces some of the carbon monoxide, resulting in formation of the [PtPh(PMePh$_2$)$_3$]$^+$ cation as well as its aroyl analogue.

Discussion

The preparation of the complex *cis*-[PtCl$_2$(CO)(PR$_3$)] described above is useful since compounds containing any one of a variety of tertiary phosphine ligands may be obtained from one common precursor. The series of tertiary phosphines employed indicates that the reaction is suitable for a range of nucleophilicities and sizes of the ligands.[15] Its limitation is reached, however, with P(*o*-tolyl)$_3$, where the extremely large ligand is apparently incapable of nucleophilic attack at the metal and no reaction of the phosphine occurs at all. That P(*o*-tolyl)$_3$ did react with [PtCl$_2$(nbd)][10] suggests that the steric constraints on this reaction are slightly greater with the cyclooctadiene complex.

The mechanism of this reaction is not immediately clear since, despite the observation of a weak electronic spectral band, the infrared and ^{13}C NMR measurements performed on solutions of [PtCl$_2$(cod)] which had been saturated with CO suggests that little interaction occurs between the complex and carbon monoxide. The extensive decomposition observed on treatment with AgBF$_4$ or TlNO$_3$, the slow reaction previously reported[4] between [PtCl$_2$(cod)] and (Et$_3$O)BF$_4$, and the air-sensitive nature of the [Pt$_2$(μ-Cl)$_2$(cod)$_2$]$^{2+}$ cation[4] suggests that chloride ion displacement by CO is unlikely, and a weak charge-transfer interaction may best account for the pink color.

Although interaction of the complex with CO is minimal, tertiary phosphine addition results in rapid formation of *cis*-[PtCl$_2$(CO)(PR$_3$)]. This implies that the initial displacement is by tertiary phosphine and that subsequent attack by CO (which is present in large excess) produces *cis*-[PtCl$_2$(CO)(PR$_3$)]. Thus, substitution by CO may only be

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possible after the chelating effect of the diolefin has been rendered inoperative. In the absence of CO, the bis(tertiary phosphine) complex is duly formed.

Kinetic studies on the displacement of 1,5-cyclooctadiene from $[Ni(C_{10}H_{12}O_2)(cod)]$ by phosphorus(III) ligands have suggested[16] that an intermediate is formed in which the diolefin functions as a monodentate ligand. Displacement of the monodentate diolefin by a second phosphorus(III) ligand is then a very rapid reaction. There is thus a precedent for sequential substitution of a bidentate olefin, which appears to be operative here in the reaction with two different incoming nucleophiles.

The diorgano complexes, on the other hand, react readily with carbon monoxide to give $[PtR_2(CO)_2]$ (R = Me or Ph). Their infrared and ^{13}C NMR data are given in Tables II and III. The ^1H NMR spectrum of $[PtMe_2(CO)_2]$ (Table IV) contains a methyl resonance very close to that of [PtMe$_2$(cod)], but the ^{13}C resonances (Table III) differ by 13.1 ppm so little may be deduced about the influences of the olefinic and carbonyl moieties on the methyl group environments in the two complexes. That these complexes are so readily formed is doubtless due to elimination of the diolefin being facilitated by the presence of the high trans influence organo ligands.[17] Spontaneous carbonyl insertion into the platinum–carbon bonds does not proceed, however, nor can it be promoted by addition of a nucleophile. Thus introduction of $PMePh_2$ to a solution of $[PtPh_2(CO)_2]$ causes displacement of coordinated CO to give *cis*-$[PtPh_2(PMePh_2)_2]$.

Carbonyl insertion does occur, however, when the monoorgano complexes, [PtClR(cod)] (R = Me or Ph), are treated with carbon monoxide. The reaction with [PtClPh(cod)] was much faster than that with the methyl analogue and, while the phenyl complex produced [PtCl(COPh)(cod)] quantitatively, the methyl compound reacted to give carbonyl species as well as [PtCl(COMe)(cod)]. While no satisfactory explanation of this behavior is apparent, it may be noted that such kinetic[12,13] and thermodynamic[14] discrepancies between phenyl and methyl groups are well-known. Low-temperature ^{13}C NMR studies of the [PtClPh(cod)]/^{13}CO system indicated the presence of intermediate terminal carbonyl species, which on warming were converted to the aroyl complex, though their exact nature could not be elucidated. Treatment of [PtClPh(cod)] with silver or thallium salts in the presence of CO caused extensive decomposition, suggesting that the cationic platinum species are inherently unstable. Addition of a catalytic amount of $AgBF_4$ to a solution of [PtClMe(cod)] in the presence of CO had no effect on the reaction (except to produce a small amount of decomposition). If halide displacement was involved such treatment should increase the rate of reaction,[18] and this observation and the instability of the cationic species suggest that chloride ion displacement is not involved. Thus the observed intermediates are more likely to be five-coordinate species, [PtClPh(CO)(cod)], or four-coordinate complexes in which one olefinic moiety has been displaced. If these reactions do indeed depend on the trans influence of the anionic ligand,[17] as seems likely, the olefinic group trans to Ph would be expected to be displaced by carbon monoxide. Unlike the diorgano complex case, however, one olefinic group would remain coordinated, and the ligand's chelating ability might be instrumental in bringing about the rearrangement to the observed product.

A number of interesting points emerge from the ^{13}C NMR spectra of the cyclooctadiene complexes. The ^{13}C chemical shifts and $^1J(Pt-C)$ values for the olefinic carbon atoms are dependent on the natures of both the cis and trans ligands. The symmetrical complexes have δ(C) values around 100 for all the olefinic carbon atoms, but in the [PtClR(cod)] complexes (R = Me, Ph or COPh) the olefinic carbons trans to R have values around δ 115 and those cis to R around δ 85 (Table III). Also, the $^1J(Pt-C)$ coupling constants for olefinic carbon atoms trans to Cl increase from 154 Hz in [PtCl$_2$(cod)] to 210 Hz, 216 Hz, and 232 Hz in [PtClR(cod)] (R = Ph, Me, and COPh, respectively). Conversely, the $^1J(Pt-C)$ values for olefinic carbon atoms trans to Ph or Me decrease on going from [PtR$_2$(cod)] to [PtClR(cod)] (Table III). Thus it appears that, in the unsymmetrical complexes, weakening of one platinum–olefin bond (by the high trans influence ligand R) results in increased strength of the other, and vice versa. A further consequence of this is that platinum–carbon coupling is observed for the methylene carbon atoms, and these values of 23–31 Hz may arise by coupling through the stronger platinum–olefin bond. It may also be noted that the $^1J(Pt-C)$ value for the olefinic carbon atoms trans to COPh is smaller than that for the carbons trans to Ph (Table III), for the corresponding [PtClR(cod)] complexes, indicating that the aroyl group exerts a greater trans influence than does the aryl group.

It was previously noted[19] that in [PtClPh(cod)] coupling of platinum to the metallated carbon of the phenyl ring was not observed, and it was suggested that this was due to the lack of any nuclear Overhauser enhancement by ^1H irradiation. In this work, the metallated carbon resonances were not observed in the phenyl complexes, and the methyl carbon resonances in the relevant complexes were also very weak. It is well-known[20] that methyl carbon atoms largely relax by spin-rotation interactions rather than by dipole–dipole interactions, and this would account for the lack of any NOE in these complexes also.

Reactions of the cyclooctadiene complexes with $PMePh_2$ all proceeded by diolefin displacement to give bis(tertiary phosphine) complexes. With [PtCl(COPh)(cod)] was also formed some $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$, suggesting that, once the chelate effect of the diolefin ligand has been removed, even a bridging chloride is able to displace the remaining olefinic group.

These reactions indicate the important roles which may be played by trans influence and chelate effects, such that the course of the reaction may be completely altered by a combination of these factors. Thus, in the reactions with CO and tertiary phosphine, the cyclooctadiene complexes yield products of a very diverse nature.

Acknowledgment. We thank Dr. A. Woon-Fat for certain of the FT NMR data. The continued financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. *cis*-[PtCl$_2$(CO)(PEt$_3$)], 65466-58-2; *cis*-[PtCl$_2$(CO)(P-*n*-Bu$_3$)], 73320-20-4; *cis*-[PtCl$_2$(CO)(PMePh$_2$)], 69109-32-6; *cis*-[PtCl$_2$(CO)(PPh$_3$)], 19618-78-1; *cis*-[PtCl$_2$(CO)(P(C$_6$H$_4$F-*p*)$_3$)], 76705-01-6; *cis*-[PtCl$_2$(CO)(P(c-Hx)$_3$)], 19618-81-6; PtCl(COPh)(cod), 76705-02-7; PtCl(COMe)(cod), 76705-03-8; PtPh$_2$(CO)$_2$, 76705-04-9; PtMe$_2$(CO)$_2$, 76705-05-0; PtCl$_2$(cod), 12080-32-9; PtClPh(cod), 51177-65-2; PtClMe(cod), 50978-00-2; PtPh$_2$(cod), 12277-88-2; PtMe$_2$(cod), 12266-92-1; *cis*-[PtCl$_2$(PMePh$_2$)$_2$], 16633-72-0; [PtCl(PMePh$_2$)$_3$]$^+$, 76740-64-2; *cis*-[PtPh$_2$(PMePh$_2$)$_2$], 51538-76-2; *trans*-[PtCl(COPh)(PMePh$_2$)$_2$], 60742-07-6; *trans*-[PtClPh(PMePh$_2$)$_2$], 60772-01-2; [Pt(COPh)(PMePh$_2$)$_3$]$^+$, 76705-06-1; [Pt(COPh)(PMePh$_2$)$_2$(acetone)]$^+$, 76705-07-2; [PtPh(PMePh$_2$)$_3$]$^+$, 76705-08-3.

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