

Preliminary communication

A REMARKABLE DEPENDENCE OF CARBON MONOXIDE INSERTION INTO A PLATINUM (II)—CARBON σ -BOND ON THE NATURE OF THE COORDINATED DITERTIARY PHOSPHINE

MARTIN A. BENNETT* and ANDRZEJ ROKICKI

Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600 (Australia)

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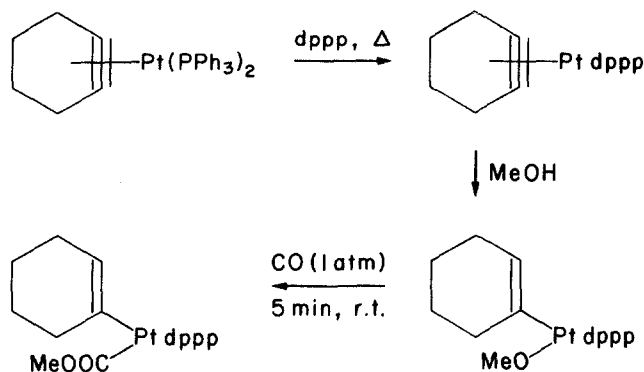
Summary

The 1-cyclohexenylmethoxycarbonyl complex $\text{Pt}(\text{CO}_2\text{Me})(\text{C}_6\text{H}_9)(\text{dppp})$ ($\text{dppp} = 1,3\text{-bis}(\text{diphenylphosphino})\text{propane}$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$) undergoes irreversible insertion of CO into the $\text{Pt}-\text{C}_6\text{H}_9$ bond under ambient conditions to give $\text{Pt}(\text{CO}_2\text{Me})(\text{COC}_6\text{H}_9)(\text{dppp})$, which may contain a *dihapto*-acyl group; the analogous 1-cyclohexenyl complexes containing 1,2-bis(diphenylphosphino)-ethane and *cis*-1,2-bis(diphenylphosphino)ethylene are unreactive under the same conditions.

Although platinum(II) complexes of the type *trans*- PtClRL_2 ($\text{R} = \text{alkyl or aryl}$; $\text{L} = \text{monodentate tertiary phosphine}$) undergo insertion of CO into the metal—carbon bond under mild conditions [1–8], similar complexes containing bidentate ligands are reported to be unreactive. Thus, there is no reaction between CO (1 atm) and PtClPhL_2 ($\text{L}_2 = \text{dppe, appe}$) or PtPh_2L_2 ($\text{L}_2 = \text{dppm, dppe, appe}$)* at room temperature after 72 h [8], and the complexes $\text{PtMe}_2(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)$ ($\text{R} = \text{Me, Et, Ph}$) react with CO only under forcing conditions (90°C, 20 atm, 6 h) to give a mixture of products; only in the case of $\text{R} = \text{Et}$ could the methyl (acetyl) complex be isolated in low yield [1].

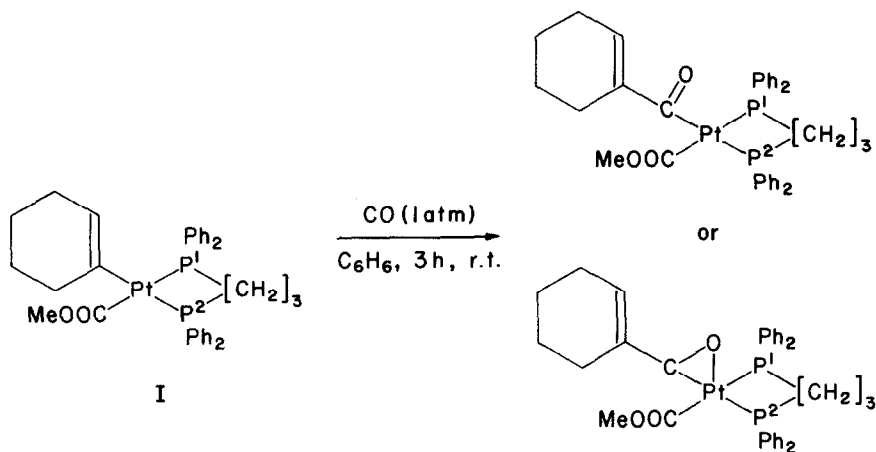
We have reported [9] that the cyclohexyneplatinum(0) complex $\text{Pt}(\text{C}_6\text{H}_8)(\text{dppe})$ reacts with methanol to form a thermally stable methoxoplatinum(II)

*Abbreviations: $\text{dppm} = \text{bis}(\text{diphenylphosphino})\text{methane}$, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$; $\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$; $\text{appe} = 1\text{-(diphenylarsino)-2-(diphenylphosphino)ethane}$, $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$; $\text{dppp} = 1,3\text{-bis}(\text{diphenylphosphino})\text{propane}$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$; $\text{vdpe} = \text{cis-1,2-bis}(\text{diphenylphosphino})\text{ethylene}$, $\text{cis-Ph}_2\text{PCH}=\text{CHPPh}_2$.



SCHEME 1

complex, $\text{Pt(OMe)(C}_6\text{H}_9\text{)(dppe)}$, which undergoes rapid insertion of CO into the Pt—O bond to give the methoxycarbonyl species $\text{Pt(CO}_2\text{Me)(C}_6\text{H}_9\text{)(dppe)}$. Unexpectedly, the similarly prepared dppp analogue (I) (Scheme 1) takes up another mol of CO (benzene, room temperature, 3 h, 1 atm) to give quantitatively the acyl complex $\text{Pt(CO}_2\text{Me)(COC}_6\text{H}_9\text{)(dppp)}$ (II) (Scheme 2). Under similar



SCHEME 2

II

conditions, the corresponding complexes $\text{Pt(CO}_2\text{Me)(C}_6\text{H}_9\text{)L}_2$ ($\text{L}_2 = \text{dppe, vdpe}$) fail to react with CO. Structural assignments are based largely on the ^{13}C NMR spectra of samples prepared by use of 90% enriched ^{13}C CO (Table 1). Both I and II exhibit a quartet at ca δ 200 ppm with ^{195}Pt satellites arising from the metallo-ester carbon atom which is coupled to *cis*- and *trans*-phosphorus atoms. The ^{13}C NMR spectrum of II shows an additional quartet with ^{195}Pt satellites at δ 240.3 ppm ($^2J(\text{CP})(\text{cis})$ 8.7 Hz, $^2J(\text{CP})(\text{trans})$ 105.5 Hz, $^1J(\text{PtC})$ 903 Hz) due to the additional carbonyl carbon. The magnitude of the Pt—C coupling constants in II establishes that both carbonyl groups are bound directly to platinum and eliminates the possibility that CO has inserted into the Pt—CO₂Me bond. This is also evident from selective ^{31}P -decoupling experiments. Irradiation of the ^{13}C NMR spectrum of II with the frequency corresponding to phosphorus

TABLE 1

¹³C^a AND ³¹P^b NMR SPECTRAL DATA FOR Pt(CO₂Me)C₆H₅(dppp) (I) AND Pt(CO₂Me)(COC₆H₅)(dppp) (II)

	I	II
δ(Pt—CO ₂ Me)	198.3	194.1
² J(CP)(<i>cis</i>)	12.9	14.8
² J(CP)(<i>trans</i>)	160.4	139.5
¹ J(PtC)	1346	1347
δ(Pt—COC ₆ H ₅)	—	240.3
² J(CP)(<i>cis</i>)	—	8.7
² J(CP)(<i>trans</i>)	—	105.5
¹ J(PtC)	—	903
δ(P ¹)	-1.8	-5.3
δ(P ²)	-7.3	-8.7
¹ J(PtP ¹)	1882	2017
¹ J(PtP ²)	1564	1415
² J(PP)	22.6	26.9

^aIn CD₂Cl₂ with internal TMS. ^bIn CH₂Cl₂ or CD₂Cl₂, δ in ppm relative to external 85% H₃PO₄ (positive to high frequency).

atom P¹ (δ -5.30 ppm rel. to 85% H₃PO₄) collapses the *trans*-coupling to the ester carbon and the *cis*-coupling to the acyl carbon, whereas decoupling of P² (δ -8.70 ppm) has the opposite effect. The magnitudes of ¹J(PtP²) in complexes I and II (Table 1) indicate that the acyl group C₆H₅CO has an even higher *trans*-influence than C₆H₅; the high *trans*-influence of acetyl is evident from X-ray structural analyses [10–12] and a comparison of the Pt—Cl bond lengths in *trans*-PtClX(PMePh₂)₂ (X = CH₃, COCH₃) indicates the *trans*-influence of acetyl to be greater than that of methyl [13,14].

The IR spectra of I and II show typical metalloester bands at ca. 1625 and 1053 cm⁻¹ due to ν(C=O) and ν(C—O—C), respectively, but that of II also shows an intense band at 1569 cm⁻¹ which must be assigned to ν(C=O) of the acyl group. This value is well below the usual range for η¹-acyls (1640–1720 cm⁻¹) and suggests the presence in II of a η²-acyl ligand (cf. Ru(η²-COC₆H₄Me-*p*)-I(CO)(PPh₃)₂ (1550 cm⁻¹) [15] and Ru(η²-COMe)I(CO)(PPh₃)₂ (1599 cm⁻¹) [16]. In contrast with η¹-acyls of the type *trans*-PtCl(COR)L₂, II does not undergo decarbonylation to I on heating in organic solvents below 100°C or on heating in vacuo in the solid state at ca. 80°C. However, on heating in *o*-dichlorobenzene or on melting in vacuo, II loses both σ-bonded groups to give unidentified products.

In solution, I undergoes exchange with gaseous ¹³CO at the metalloester group before appreciable insertion into the Pt—C₆H₅ bond has occurred. This process probably involves reversible dissociation of methoxide ion from I to give the cation [Pt(C₆H₅)(CO)(dppp)]⁺ which can then exchange with ¹³CO via a five-coordinate dicarbonyl; reversible dissociation of methoxide from a metalloester has been demonstrated in the case of Fe(η-C₅H₅)(CO₂Me)(CO)(PPh₃) [17]. Complex II also exchanges with ¹³CO at the metalloester group but no label appears at the acyl position, showing that insertion of CO into the Pt—C₆H₅ bond of I is irreversible.

The remarkable ability of dppp relative to other ditertiary phosphines to promote insertion of CO into a platinum(II)—carbon σ -bond has parallels in rhodium(I) chemistry. Thus, $[\text{Rh}(\text{dppp})_2]\text{BF}_4$ readily adds CO to give five-coordinate $[\text{Rh}(\text{CO})(\text{dppp})_2]\text{BF}_4$ and dihydrogen to give six-coordinate $[\text{RhH}_2(\text{dppp})_2]\text{BF}_4$, whereas $[\text{Rh}(\text{dppe})_2]\text{BF}_4$ is inert to both reagents [18,19]. In the series $[\text{Rh}(\text{L}_2)_2]\text{BF}_4$, the order of catalytic activity for decarbonylation of benzaldehyde to benzene is $\text{L}_2 = \text{dppp} > \text{dppe} > \text{dppm}, \text{dppb}$ [20].

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