Journal of Organometallic Chemistry, 244 (1983) C31–C34
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

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)

(Received November 23rd, 1982)

Summary

The 1-cyclohexenylmethoxycarbonyl complex $Pt(CO_2Me)(C_6H_9)(dppp)$ (dppp = 1,3-bis(diphenylphosphino)propane, $Ph_2PCH_2CH_2CH_2PPh_2$) undergoes irreversible insertion of CO into the $Pt–C_6H_9$ bond under ambient conditions to give $Pt(CO_2Me)(COC_6H_9)(dppp)$, 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.

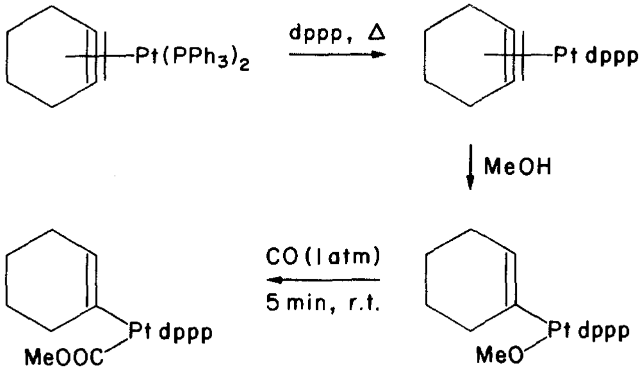
Although platinum(II) complexes of the type *trans*-$PtClRL_2$ (R = alkyl or aryl; L = monodentate tertiary phosphine) undergo insertion of CO into the metal–carbon bond under mild conditions [1–8], similar complexes containing bidentate ligands are reported to be unreactive. Thus, there is no reaction between CO (1 atm) and $PtClPhL_2$ (L_2 = dppe, appe) or $PtPh_2L_2$ (L_2 = dppm, dppe, appe)* at room temperature after 72 h [8], and the complexes $PtMe_2(R_2PCH_2CH_2PR_2)$ (R = 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 R = Et could the methyl (acetyl) complex be isolated in low yield [1].

We have reported [9] that the cyclohexyneplatinum(0) complex $Pt(C_6H_8)$-(dppe) reacts with methanol to form a thermally stable methoxoplatinum(II)

---

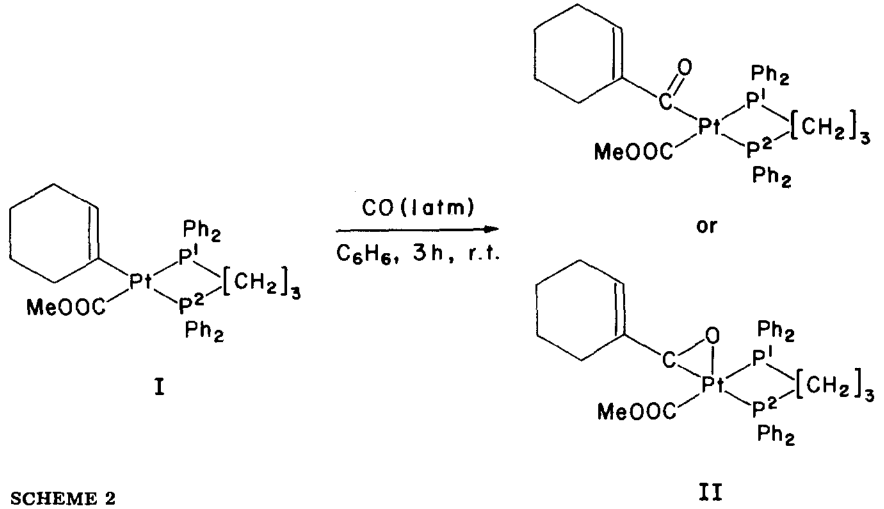
*Abbreviations: dppm = bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$; dppe = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$; appe = 1-(diphenylarsino)-2-(diphenylphosphino)ethane, $Ph_2AsCH_2CH_2PPh_2$; dppp = 1,3-bis(diphenylphosphino)propane, $Ph_2PCH_2CH_2CH_2PPh_2$; vdpe = *cis*-1,2-bis(diphenylphosphino)ethylene, *cis*-$Ph_2PCH{=}CHPPh_2$.

0022-328X/83/0000–0000/$03.00



SCHEME 1

complex, Pt(OMe)(C_6H_9)(dppe), which undergoes rapid insertion of CO into the Pt—O bond to give the methoxycarbonyl species Pt(CO_2Me)(C_6H_9)(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 Pt(CO_2Me)(COC_6H_9)(dppp) (II) (Scheme 2). Under similar conditions, the corresponding complexes Pt(CO_2Me)(C_6H_9)L_2 (L_2 = 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}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(CP)(*cis*) 8.7 Hz, ^2J(CP)(*trans*) 105.5 Hz, ^1J(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—CO_2Me 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



SCHEME 2

TABLE 1

$^{13}C^{a}$ AND $^{31}P^{b}$ NMR SPECTRAL DATA FOR $Pt(CO_2Me)C_6H_9)(dppp)$ (I) AND $Pt(CO_2Me)(COC_6H_9)$-(dppp) (II)

	I	II
$\delta(Pt—CO_2Me)$	198.3	194.1
$^2J(CP)$(*cis*)	12.9	14.8
$^2J(CP)$(*trans*)	160.4	139.5
$^1J(PtC)$	1346	1347
$\delta(Pt—COC_6H_9)$	—	240.3
$^2J(CP)$(*cis*)	—	8.7
$^2J(CP)$(*trans*)	—	105.5
$^1J(PtC)$	—	903
$\delta(P^1)$	−1.8	−5.3
$\delta(P^2)$	−7.3	−8.7
$^1J(PtP^1)$	1882	2017
$^1J(PtP^2)$	1564	1415
$^2J(PP)$	22.6	26.9

[a] In CD_2Cl_2 with internal TMS. [b] In CH_2Cl_2 or CD_2Cl_2, δ in ppm relative to external 85% H_3PO_4 (positive to high frequency).

atom P^1 (δ −5.30 ppm rel. to 85% H_3PO_4) collapses the *trans*-coupling to the ester carbon and the *cis*-coupling to the acyl carbon, whereas decoupling of P^2 (δ −8.70 ppm) has the opposite effect. The magnitudes of $^1J(PtP^2)$ in complexes I and II (Table 1) indicate that the acyl group C_6H_9CO has an even higher *trans*-influence than C_6H_9; 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*-$PtClX(PMePh_2)_2$ (X = CH_3, $COCH_3$) 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 $\nu(C{=}O)$ and $\nu(C—O—C)$, respectively, but that of II also shows an intense band at 1569 cm^{-1} which must be assigned to $\nu(C{=}O)$ of the acyl group. This value is well below the usual range for η^1-acyls (1640—1720 cm^{-1}) and suggests the presence in II of a η^2-acyl ligand (cf. $Ru(\eta^2\text{-}COC_6H_4Me\text{-}p)I(CO)(PPh_3)_2$ (1550 cm^{-1}) [15] and $Ru(\eta^2\text{-}COMe)I(CO)(PPh_3)_2$ (1599 cm^{-1}) [16]. In contrast with η^1-acyls of the type *trans*-$PtCl(COR)L_2$, 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 ^{13}CO at the metalloester group before appreciable insertion into the $Pt—C_6H_9$ bond has occurred. This process probably involves reversible dissociation of methoxide ion from I to give the cation $[Pt(C_6H_9)(CO)(dppp)]^+$ which can then exchange with ^{13}CO via a five-coordinate dicarbonyl; reversible dissociation of methoxide from a metalloester has been demonstrated in the case of $Fe(\eta\text{-}C_5H_5)(CO_2Me)(CO)(PPh_3)$ [17]. Complex II also exchanges with ^{13}CO at the metalloester group but no label appears at the acyl position, showing that insertion of CO into the $Pt—C_6H_9$ 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, $[Rh(dppp)_2]BF_4$ readily adds CO to give five-coordinate $[Rh(CO)(dppp)_2]BF_4$ and dihydrogen to give six-coordinate $[RhH_2(dppp)_2]BF_4$, whereas $[Rh(dppe)_2]BF_4$ is inert to both reagents [18,19]. In the series $[Rh(L_2)_2]BF_4$, the order of catalytic activity for decarbonylation of benzaldehyde to benzene is L_2 = dppp > dppe > dppm, dppb [20].

References

1 G. Booth and J. Chatt, J. Chem. Soc. A, (1966) 634.
2 C.J. Wilson, M. Green and R.J. Mawby, J. Chem. Soc. Dalton Trans., (1974) 421, 1293.
3 P.E. Garrou and R.F. Heck, J. Amer. Chem. Soc., 98 (1976) 4115.
4 N. Sugita, J.V. Minkiewicz and R.F. Heck, Inorg. Chem., 17 (1978) 2809.
5 G.K. Anderson and R.J. Cross, J. Chem. Soc. Dalton Trans., (1979) 1246; (1980) 1434.
6 R.J. Cross and J. Gemmill, J. Chem. Soc. Dalton Trans., (1981) 2317.
7 G.K. Anderson, H.C. Clark and J.A. Davies, Inorg. Chem., 20 (1981) 1636.
8 G.K. Anderson, H.C. Clark and J.A. Davies, Inorg. Chem., 20 (1981) 3607.
9 M.A. Bennett and T. Yoshida, J. Amer. Chem. Soc., 100 (1978) 1750.
10 G. Huttner, O. Orama and V. Bejenke, Chem. Ber., 109 (1976) 2533.
11 R. Bardi, A. Del Pra, A.M. Piazzesi and L. Toniolo, Inorg. Chim. Acta, 35 (1979) L35.
12 G.K. Anderson, R.J. Cross, L. Manojlović-Muir, K.W. Muir and T. Solomun, J. Organometal. Chem., 170 (1979) 385.
13 M.A. Bennett, Ho Kin-Chee and G.B. Robertson, Inorg. Chem., 18 (1979) 1061.
14 M.A. Bennett, Kin-Chee Ho, J.C. Jeffery, G.M. McLaughlin and G.B. Robertson, Aust. J. Chem., 35 (1982) 1311.
15 W.R. Roper and L.J. Wright, J. Organometal. Chem., 142 (1977) C1.
16 W.R. Roper, G.E. Taylor, J.M. Waters and L.J. Wright, J. Organometal. Chem., 182 (1979) C46.
17 N. Grice, S.C. Kao and R. Pettit, J. Amer. Chem. Soc., 101 (1979) 1627.
18 B.R. James and D. Mahajan, Can. J. Chem., 58 (1980) 996, and ref. cited therein.
19 D.A. Slack, I. Greveling and M.C. Baird, Inorg. Chem., 18 (1979) 3125.
20 D.H. Doughty, M.P. Anderson, A.L. Casalnuovo, M.F. McGuiggan, C.C. Tso, H.H. Wang and L.H. Pignolet, Adv. Chem. Ser., 196 (1982) 65.