place by exposure of a solution of 3 to air but is accelerated by addition of acids, or even $Na^+PF_6^-$ and occurred within seconds when H_2O_2 was added to 3. During the reduction of **1b** with sodium amalgam, the formation of Na^+ cations may assist the elimination of the $Fe(CO)_2PPh_3$ fragment and accelerate the transformtion 3 → 4.

The present study suggests that previous examples of C–C bond formation between two metal–heteroallene moieties **7a,b**, which gave rise to the formation of another type of binuclear complex, could also be promoted by a radical process.

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Registry No. 1b, 71004-19-8; **3**, 97390-97-1; **4**, 97390-96-0; **5**, 97403-35-5; $NaBH_4$, 16940-66-2; C, 7440-44-0.

Supplementary Material Available: Tables of atomic potential and thermal parameters, interatomic distances and angles, and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

Mechanism of CO Insertion into Metal–Oxygen Bonds. Reaction of (DPPE)Pt(OCH$_3$)R (R = CH$_3$ or OCH$_3$) with CO[†]

Henry E. Bryndza

Central Research & Development Department
Experimental Station, E. I. du Pont de Nemours & Company
Wilmington, Delaware 19898

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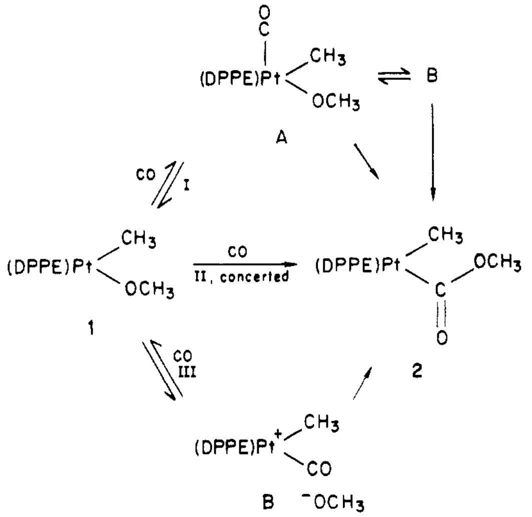
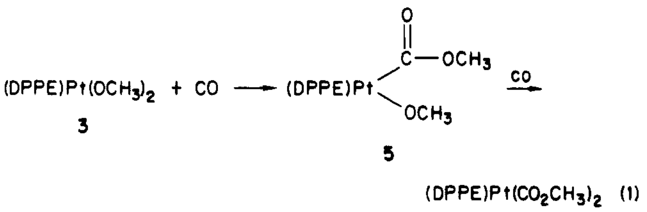
Summary: The carbonylation of $(DPPE)PtCH_3(OCH_3)$, **1** (DPPE = 1,2-bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$), to yield $(DPPE)PtCH_3(CO_2CH_3)$ is first order in **1** and first order in CO. Low-temperature ^{13}C NMR experiments suggest formation of a five-coordinate CO complex intermediate, and crossover experiments rule out the involvement of dissociated species during this reaction. Similar complex **3**, $(DPPE)Pt(OCH_3)_2$, carbonylates stepwise through $(DPPE)Pt(OCH_3)(CO_2CH_3)$ to ultimately form $(DPPE)Pt(CO_2CH_3)_2$. Similar kinetics and alcohol exchange reactions suggest the carbonylation mechanism is the same one outlined for the methyl methoxide. Low-temperature ^{13}C NMR measurements permit observation and quantification of a five-coordinate CO adduct.

During our investigation of reactions relevant to the palladium-catalyzed carbonylation of alcohols to dialkyl oxalates, we found platinum alkoxide 1 carbonylates to carbomethoxide complex **2**. Similarly, we observed related bis alkoxide **3** reacts with CO to give bis(carbomethoxide) **4** through the intermediacy of complex **5**.[1,2] While carboalkoxide formation from carbonylation of platinum alkoxides has been known for some time,[3] the mechanism has not been explored. We now show the mechanism of carboalkoxide formation for 1 involves inner-sphere insertion of CO into the metal-oxygen bond and most probably proceeds through the formation of a five-coordinate CO complex.

Scheme I



$$\underset{\mathbf{1}}{(DPPE)PtCH_3(OCH_3)} + CO \rightarrow \underset{\mathbf{2}}{(DPPE)PtCH_3(CO_2CH_3)}$$



3 **5** **4**

$$\underset{\mathbf{3}}{(DPPE)Pt(OCH_3)_2} + CO \rightarrow \underset{\mathbf{5}}{(DPPE)Pt(C(=O)OCH_3)(OCH_3)} \xrightarrow{CO} \underset{\mathbf{4}}{(DPPE)Pt(CO_2CH_3)_2} \quad (1)$$

Carbonylation of 1 was followed by ^1H and ^{31}P NMR[4] at −20 °C. The reaction is first order in 1 to better than 3 half-lives. With use of CO pressures ranging from 0 to 150 psi, the observed rate was found to be first order in the concentration of CO.[5] This first-order CO dependence suggests this reaction does not proceed by initial dissociation of methoxide; this expectation was confirmed by putting an upper limit on the rate of methanol dissociation from 1 that is 3 orders of magnitude slower than the observed carbonylation rates.[6]

[†] Contribution No. 3562.

[1] Bryndza, H. E.; Kretchmar, S. A.; Tulip, T. H. *J. Chem. Soc., Chem. Commun.*, in press.

[2] Complex 5 was observed during the reaction of 3 and CO which ultimately yields complex 4. The concentration of 5 is effectively steady state, suggesting it is an intermediate in the production of 4.

[3] (a) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750–9. (b) Michelin, R. H.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *175*, 239–55. (c) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941-2. (d) Appleton, T. G.; Bennett, M. A. *J. Organomet. Chem.* **1973**, *55*, C89.

[4] In a typical experiment, a pressure NMR tube was loaded in a drybox with a THF-d_8 or CD_2Cl_2 solution of 1 and charged to gauge pressures with CO.

[5] The rate of reaction is described by the following relationship: $-d[1]/dt = d[2]/dt = k[1][CO]$ where, in CD_2Cl_2, $k = 4.1 \times 10^{-2}\ s^{-1}\ mol^{-1}$ at −20 °C. The concentration of CO in solution was determined by preparing known concentration solutions of ^{13}C-enriched benzaldehyde (90% enrichment in the carbonyl position) and sealing the system with a known pressure of ^{13}CO (also 90% enrichment). The concentration of CO at 1 atm of CO pressure in CD_2Cl_2 is expressed by

$$[CO]_{1\,atm} = 2.75 \times 10^{-6}(T) + 6.45 \times 10^{-3}$$

where [CO] is in molarity and T is in °C over the range of +30 to −80 °C.

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While these observations rule out predissociation of methoxide, three kinetically indistinguishable mechanisms for the overall conversion of **1** to **2** must still be considered. They are (Scheme I) (I) precoordination of CO to **1** followed by insertion of CO into the metal–oxygen bond of A, (II) an unprecedented concerted insertion of CO into the metal–oxygen bond, and (III) the displacement of methoxide by CO to form charged intermediates B, which may revert to starting materials or be converted to product **2**.

When **1** was combined with ^{13}CO from −20 to −100 °C, a very broad single resonance was observed at 184 ppm in the ^{13}C NMR spectrum, suggesting some pre-equilibrium interaction of **1** and ^{13}CO takes place prior to forming **2**. During this apparently rapid process, no loss of ^{195}Pt coupling to either the methoxide protons or the DPPE phosphorous nucleii is observed.

Consistent with this observation, when related complex **3** was combined with ^{13}CO under the same conditions, two resonances were observed which correspond to free ^{13}CO and a new complex of **3** and ^{13}CO as evidenced by ^{195}Pt satellites.[7] The new complex shows no large ^{31}P to ^{13}C coupling, and the two methoxide groups remain equivalent by ^{1}H NMR.[8] Warming the solution changes the distribution[9] of these signals in favor of free CO until at −20 °C the two signals coalesce making further quantification impossible. Together these observations suggest the first step of carbonylation may be pre-equilibrium coordination of CO to form intermediate A.

While dissociation of methoxide from **1** is clearly very slow, the same cannot be assumed for A. In order to determine the molecularity of the overall carbonylation reaction, a crossover experiment was carried out in which **1** was combined with 15 equiv of CD_3OD and 10 atm of CO; NMR analysis of product **2** showed less than 5% OCD_3 groups. Independent measurements of the carbonylation and methanol exchange rates of **1**[6] and the crossover dependence on CO pressure[10] suggest that even this small amount of observed crossover is accounted for by exchange of **1** and CD_3OD. To the accuracy of our experiments, this result shows methoxide does not dissociate from **1** at any time during carbomethoxide synthesis and we suggest the same may be true for **3** and **5**.[11] Together these observations show CO can coordinate to platinum(II) alkoxides in preequilibrium fashion which can be followed by a rate-limiting inner-sphere insertion of CO into an available metal–oxygen bond.[12]

Several interesting aspects are worth mentioning. In complex **1**, CO inserts into the Pt–O bond without our ever observing insertion into the available Pt–C bond in the same molecule.[13] Similarly, in complex **5** the second metal–oxygen bond reacts with CO in preference to the available sp^2 metal–carbon bond. This second carbonylation is faster than the first as **5** never builds up to more than a few percent during this reaction.[14]

This insertion mechanism is analogous to those previously established for insertion of CO into metal–carbon bonds;[15] it demonstrates that outer sphere processes need not be invoked to explain the reactions of late transition metal–oxygen bonds.[16] The implications of these results to the overall mechanism of oxalate ester synthesis will be reported elsewhere as will the general implications of these results to the reactivity of late transition metal–carbon, –nitrogen, and –oxygen bonds.

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Registry No. **1**, 82405-05-8; **2**, 91993-69-0; **3**, 97295-81-3; **4**, 97295-82-4; **5**, 97295-83-5; (DPPE)$PtCH_3(OCH_3)(CO)$, 97295-84-6; CO, 630-08-0.

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[6] Psuedo-first-order exchange of 10 equiv of CD_3OD with **1** and **3** shows $-d[PtOCH_3]/dt = k[PtOCH_3][CD_3OD]$; this result requires nondissociative methanol exchange with the error in the intercept of a k_{obsd} vs. $[CD_3OD]$ plot corresponding to the maximum rate of methoxide dissociation. For both **1** and **3**, this rate is less than 10^{-7} s^{-1}. While methoxide dissociation from **1** is more than 10^3 slower than the rate of carbonylation, overall methanol exchange is only a factor of 9 slower than carbonylation at 5 atm of CO pressure.

[7] ^{13}C parameters (CD_2Cl_2/CH_2Cl_2) at −80 °C: 184.9 (s) ppm; J_{CPt} = 1753 Hz; line width = 17 Hz.

[8] These observations suggest a square-pyramidal ground state with apical CO for the five-coordinate CO adduct.

[9] Thermodynamic parameters measured: $\Delta H^{\ddagger} = -7.4 \pm 0.1$ kcal/mol, $\Delta S^{\ddagger} = -26 \pm 3$ eu. Temperature range: −75 to −25 °C.

[10] Crossover was determined by integration of CH_3OD vs. $PtCO_2CH_3$ resonances (accuracy of the reported figure is 5% +0, −2%). At lower CO pressures, larger extents of crossover is noted (12% at 5 atm). The crossover dependence on $[DOCD_3]$ and on CO pressure shows that, within our experimental error, carbonylation is a completely intramolecular insertion process from A.

[11] Because associative methanol exchange is faster than associative carbonylation for **3**, similar crossover experiments could not be run with this complex. However, the similarity of carbonylation kinetics and methanol exchange for **1** and **3** suggest the mechanism of carbonylation of **3** and **5** are similar to that investigated for **1**. NMR and X-ray crystallographic data show **1** and **3** are very similar, structurally.

[12] Our experiments cannot distinguish between the involvement of a polar M–O bond and a contact ion pair in A, the difference between which is more semantic than practically significant. Since any charge separation along the reaction coordinate must be so transient as to exclude the faster than diffusion controlled deuteron scrambling with CD_3OD solvent, we think of this reaction as involving a polar transition state. Clearly OR ligands do not leave the Pt coordination sphere during insertion prior to actual O–C bond formation. This situation is analogous to the generally accepted mechanism for alkyl migration to coordinated CO; polar M–C bonds do, at some point, break as new C–C bonds form. Other experiments show similar five-coordinate (DPPE)$PtR(OCH_3)(CH_3OH)$ complexes ($R = CH_3$, OCH_3) fail to react with esters or ethylene oxide in THF/methanol solutions. This suggests ion pairs are not accessible in these systems.

[13] (a) Bennett, M. A.; Rokicki, A. *Organometallics* **1985**, *4*, 180–187. (b) Bennett, M. A.; Rokicki, A. *J. Organomet. Chem.* **1983**, *244*, C31.

[14] No evidence for an α,β-dicarbonyl product is seen. To the contrary, in other systems the decarbonylation of such species is rapid. In addition, the importance of bis(carbomethoxide) complexes in the synthesis of oxalate esters by Pd catalysts is inferred in other work, e.g.: (a) Rivetti, F.; Romano, U. *J. Organomet. Chem.* **1978**, *154*, 323–326. (b) Rivetti, F.; Romano, U. *J. Organomet. Chem.* **1979**, *174*, 221–6. (c) Burk, P. L.; Van Engen, P.; Campo, K. S. *Organometallics* **1984**, *3*, 493–5. (d) Fendon, P. M.; Steinwald, P. J. *J. Org. Chem.* **1974**, *39*, 701–704. (e) Rivetti, F.; Romano, U. *Chim. Ind.* (*Milan*) **1980**, *62*, 7–12.

[15] For leading references see "Principles and Applications of Organotransition Metal Chemistry"; Collman, Hegedus, Eds.; University Science Books: Mill Valley, CA, 1980; pp 260–288. This reported insertion reaction shows the general coordination followed by insertion behavior evident in reactions of CO with M–C bonds.

[16] A communication by W. M. Reese and J. D. Atwood (*Organometallics* **1985**, *4*, 402–4) reported generation of charged species on addition of CO to $ROIr(CO)(PPh_3)_2$ at low temperature. It was not yet possible to determine if these ions are on the reaction path to the ultimate $RO_2ClIr(CO)_2(PPh_3)_2$ products.

(Chloromethyl)lithium: Efficient Generation and Capture by Boronic Esters and a Simple Preparation of Diisopropyl (Chloromethyl)boronate

Kizhakethil Mathew Sadhu and Donald S. Matteson*

Department of Chemistry, Washington State University
Pullman, Washington 99164-4630

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Summary: (Chloromethyl)lithium is efficiently generated and captured at −78 °C by adding *n*-butyllithium to a