Insertion of CO into a CH_3-Pd Bond in a Heterodinuclear Complex (dpe)MePd-Co(CO)$_4$. Preferential Insertion of Coordinated CO on a Cobalt Moiety

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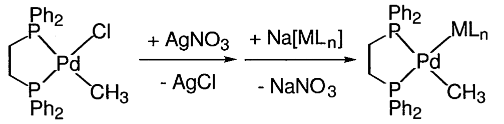
A palladium-containing heterodinuclear complex (dpe)MePd-Co(CO)$_4$ shows higher reactivity toward CO insertion than PdMeCl(dpe) and (dpe)MePt-Co(CO)$_4$ to give an acetyl complex (dpe)AcPd-Co(CO)$_4$. The insertion of CO ligand in Co(CO)$_4$ is a kinetically favorable process.

Heterodinuclear complexes have attracted much attention, since they may show cooperative effect of different metal centers on the reactivities of organic ligands such as alkyl and aryl groups.[1] We have reported the enhancement of reductive elimination and ß-H elimination on Pt-containing heterodinuclear complexes $L_2RPt\text{-}ML_n$ (L_2 = cod, dpe; R = alkyl, aryl; ML_n = MoCp(CO)$_3$, WCp(CO)$_3$, Mn(CO)$_5$, FeCp(CO)$_2$, Co(CO)$_4$).[2] In this work, Pd-containing heterodinuclear complexes with a methyl group have been synthesized and characterized, and their reactivity toward CO insertion has been investigated.

Metathetical reactions of PdMe(NO_3)(dpe), prepared in situ from PdMeCl(dpe) and $AgNO_3$, with slight excess Na[ML_n] in THF at -30 °C under N_2 gave new dinuclear complexes **1**-**3** (Eq. 1).[3] By comparing spectroscopic and analytical data of **1**-**3** with those of related Pt analogues (dpe)MePt-ML_n,[2c] it is suggested that **1**-**3** have a similar dinuclear structure with a Me group on Pd as shown in Eq. 1.



(1)

ML_n = MoCp(CO)$_3$ (**1**), WCp(CO)$_3$ (**2**), Co(CO)$_4$ (**3**)

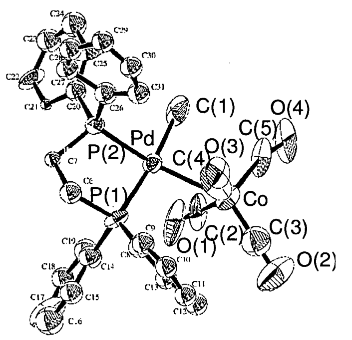


Figure 1. Molecular structure of (dpe)MePd-Co(CO)$_4$ (**3**). Selected bond distances (Å) and angles (deg): Pd-Co 2.682(8), Pd-C(1) 2.07(3), Co-Pd-C(1) 85(1), Co-Pd-P(1) 100.6(4), P(1)-Pd-P(2) 86.1(4), C(1)-Pd-P(2) 87(1).

X-ray structure analyses of **3** and its Pt analogue (dpe)MePt-Co(CO)$_4$[2c] (**4**) were performed, and the ORTEP drawing of **3** is shown in Figure 1.[4] The Pd-Co distance is 2.682(8) Å, indicating the presence of a Pd-Co single bond. The geometries at Pd and Co are square planar and distorted trigonal bipyramidal, respectively. The X-ray analysis of **4** gave almost the same results to those of **3**.[4] Among the carbonyl ligands on Co in **3** and **4**, two of them are assigned to bent semibridging carbonyls (Figure 2).[5] In particular, the C(4)-O(3) carbonyl in **3** has stronger interaction with Pd; the Pd-C(4) distance of 2.49(6) Å is shorter than those for other bent semibridging carbonyls (2.64(2)-2.67(8) Å).[6]

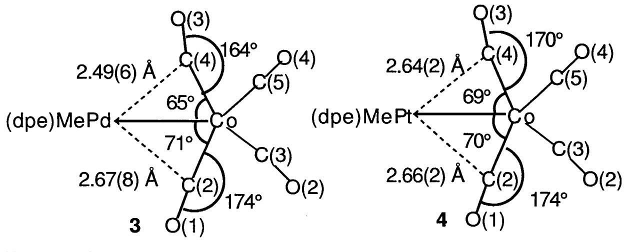
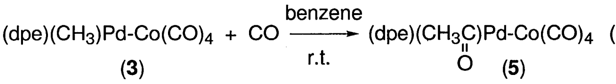


Figure 2. Bent semibridging carbonyls in **3** and **4**.

The reactivity of the new complexes toward CO insertion was studied. Treatment of **3** with CO (1 atm) in C_6D_6 at r.t. led to the formation of (dpe)AcPd-Co(CO)$_4$ (**5**) (80%) in 24 h (Eq. 2).[7,8] Under the same reaction conditions, **1** gave (dpe)AcPd-MoCp(CO)$_3$ (22%) and MeMoCp(CO)$_3$ (27%), the latter being formed from reductive elimination. In contrast, no CO insertion took place for **2**, but MeWCp(CO)$_3$ was quantitatively obtained.



$$\underset{(\mathbf{3})}{\mathrm{(dpe)(CH_3)Pd\text{-}Co(CO)_4}} + \mathrm{CO} \xrightarrow[\text{r.t.}]{\text{benzene}} \underset{(\mathbf{5})}{\mathrm{(dpe)(CH_3\underset{\underset{O}{\|}}{C})Pd\text{-}Co(CO)_4}} \quad (2)$$

To compare the reactivity of Co-containig complexes, the reactions were performed in CD_2Cl_2 in NMR tubes at 24 °C under CO (1 atm, ca. 7-fold excess). Figure 3 shows time-yield curves of CO insertion to give corresponding acetyl complexes. Pd-Co complex **3** gave much higher reactivity than mononuclear PdMeCl(dpe) (**6**) and Pt-Co complex **4**. No reaction occurred for PtMeCl(dpe). Previously reported formation of $(Me_3P)_2$-(PhC(O))Pd-Co(CO)$_4$ from PdPh(OTf)(PMe_3)$_2$ and K[Co-(CO)$_4$] even under N_2 may arise from the similar facile CO insertion.[9]

When **3** in C_6H_6 was treated with ^{13}CO (27-fold excess, 99% ^{13}C) in a Schlenk tube at r.t., the acetyl complex (**5***) was isolated in 82% yield in 6 h (Eq. 3).[10] The ^{13}C content of the acetyl CO carbon was evaluated by IR and NMR. In the IR spectrum of **5***, the $^{12}C/^{13}C$ ratio of the acetyl CO was 2.5. In the $^{31}P\{^1H\}$ NMR spectrum of **5***, the signal of P trans to the acetyl showed a coupling with ^{13}C, and the $^{12}C/^{13}C$ ratio was 2.0, being in accord with the result by IR. Since the statistical redistribution of ^{12}CO and ^{13}CO during the reaction would give a value of approximately 0.15 for the $^{12}C/^{13}C$ ratio (4 ^{12}CO in Co(CO)$_4$ and 27 ^{13}CO in the gas phase), the above data strongly suggest that CO in Co(CO)$_4$ preferentially inserts into the Me-Pd bond over ^{13}CO in the gas phase, and that scrambling is slower than CO insertion.

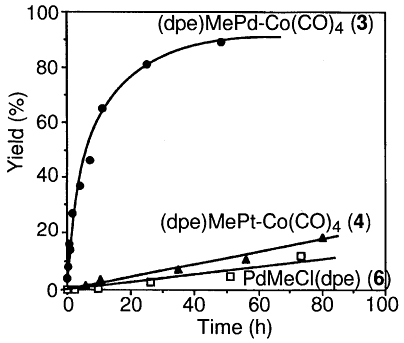
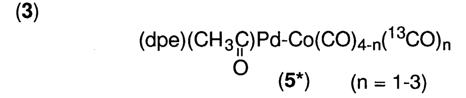


Figure 3. Time-yield curves of CO insertion.
Conditions: CD_2Cl_2, 24±1 °C, CO (1 atm, ca. 7-fold excess).



$$\mathrm{(dpe)(CH_3)Pd\text{-}Co(CO)_4}\ \underset{(\mathbf{3})}{} + {}^{13}\mathrm{CO} \xrightarrow[\text{r.t.}]{\text{benzene}} \mathrm{(dpe)(CH_3\underset{\overset{\|}{O}}{C})Pd\text{-}Co(CO)_{4-n}(^{13}CO)_n} \quad (\mathbf{5^*}) \quad (n = 1\text{-}3) \qquad (3)$$

We tentatively propose the mechanism of CO insertion under ^{13}CO atmosphere. The bent semibridging CO ligand on Co migrates to the fifth coordination site on the Pd center, resulting in the migratory CO insertion and subsequent coordination of ^{13}CO to Co. The involvement of $^{13}C(O)CH_3$ in the acetyl group may be due to the direct attack of ^{13}CO to Pd or scrambling of gaseous ^{13}CO with the CO ligand on Co, but they are kinetically minor processes.[11] Further mechanistic study is in progress.

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References and Notes

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3 **1**: yellow-brown needles from toluene/hexane; yield 38%; mp 122 °C(dec.); molar electric conductivity Λ (THF, 24 °C) 0.0069 S cm^2 mol^{-1}. Anal. Found: C, 55.35; H, 4.48%. Calcd for $C_{35}H_{32}O_3P_2$-MoPd: C, 54.96; H, 4.22%. IR (KBr, cm^{-1}) 1901, 1792 (ν_{CO}). ^{1}H NMR (C_6D_6): δ 1.52 (dd, $^3J_{PH}$ = 6.0, 7.8 Hz, 3H, Me), 1.7-1.8 (m, 4H, dpe CH_2), 4.69 (s, 5H, Cp), 7.0-7.8 (m, dpe Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 35.4 (d, $^2J_{PP}$ = 18 Hz), 56.8 (d, $^2J_{PP}$ = 18 Hz).
2: yellow-brown needles from toluene/hexane; yield 29%; mp 108 °C(dec.); Λ (THF, 24 °C) 0.0038 S cm^2 mol^{-1}. This complex was identified by the spectroscopic methods. IR (KBr, cm^{-1}) 1893, 1785 (ν_{CO}). ^{1}H NMR (C_6D_6): δ 1.69 (t, $^3J_{PH}$ = 6.9 Hz, 3H, Me), 1.6-1.7 (m, 4H, dpe CH_2), 4.64 (s, 5H, Cp), 6.9-7.8 (m, dpe Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 38.2 (d, $^2J_{PP}$ = 18 Hz), 60.7 (d, $^2J_{PP}$ = 18 Hz).
3: red cubes from benzene/hexane; yield 48%; mp 123 °C(dec.); Λ (THF, 24 °C) 0.017 S cm^2 mol^{-1}. Anal. Found: C, 53.98; H, 3.96%. Calcd for $C_{31}H_{27}O_4P_2CoPd$: C, 53.90; H, 3.94%. IR (KBr, cm^{-1}) 2020, 1953, 1913, 1885 (ν_{CO}). ^{1}H NMR (C_6D_6): δ 1.21 (dd, $^3J_{PH}$ = 5.0, 7.7 Hz, 3H, Me), 1.6-1.9 (m, 4H, dpe CH_2), 7.0-7.6 (m, dpe Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 37.2 (d, $^2J_{PP}$ = 26 Hz), 49.4 (d, $^2J_{PP}$ = 26 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 9.8 (d, J_{PC} = 106 Hz, Me), 27.8 (dd, J_{PC} = 16, 24 Hz, dpe CH_2), 29.2 (dd, J_{PC} = 22, 26 Hz, dpe CH_2), 129-134 (m, dpe Ph), 210 (br s, CO).

4 Crystal data for **3**: $C_{31}H_{27}O_4P_2CoPd$, FW = 690.83, monoclinic, $P2_1/n$ (#14), a = 10.782(8), b = 17.681(6), c = 15.950(7) Å, β = 103.59(4)°, V = 2955(2) Å^3, Z = 4, D_{calc} = 1.552 g cm^{-3}, R = 0.073, R_W = 0.045, 7052 unique reflections with $I > 3\sigma(I)$.
Crystal data for **4**: $C_{31}H_{27}O_4P_2CoPt$, FW = 779.52, monoclinic, $P2_1/n$ (#14), a = 10.741(6), b = 17.716(7), c = 15.982(5) Å, β = 103.56(3)°, V = 2956(2) Å^3, Z = 4, D_{calc} = 1.751 g cm^{-3}, R = 0.049, R_W = 0.038, 5421 unique reflections with $I > 3\sigma(I)$.

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6 No characteristic peaks of the bent semibridging CO were observed in IR and/or $^{13}C\{^1H\}$ NMR of **1**-**3**. However, as X-ray structure analysis of (cod)PhPt-MoCp$(CO)_3$ showed the presence of them,[2d] it is expected that **1** and **2** also have the bent semibridging CO.

7 **5**: yellow-brown needles from THF/hexane; yield 85%; mp 118 °C(dec.); Λ (THF, 24 °C) 0.18 S cm^2 mol^{-1}. Anal. Found: C, 53.43; H, 3.88%. Calcd for $C_{32}H_{27}O_5P_2CoPd$: C, 53.47; H, 3.79%. IR (KBr, cm^{-1}) 2025, 1951, 1919, 1893, 1680(ν_{CO}). ^{1}H NMR (C_6D_6): δ 2.27 (s, 3H, C(O)CH_3), 1.6-1.9 (m, 4H, dpe CH_2), 7.0-7.6 (m, dpe Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 24.1 (d, $^2J_{PP}$ = 45 Hz), 26.0 (d, $^2J_{PP}$ = 45 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 25.4 (dd, J_{PC} = 14, 23 Hz, dpe CH_2), 27.3 (dd, J_{PC} = 19, 27 Hz, dpe CH_2), 39.1 (dd, J_{PC} = 21, 42 Hz, CH_3), 129-134 (m, dpe Ph), 209-212 (m, CO), 235.0 (dd, J_{PC} = 12, 115 Hz, *C*(O)CH_3).

8 The reaction of **5** with 5 equiv. of $HNEt_2$ in C_6D_6 at 50 °C for 24 h gave $AcNEt_2$ in 15% yield.

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10 Selected spectroscopic data for **5***: IR (KBr, cm^{-1}) 2002, 1976, 1901, 1875, 1855, 1818, 1674, 1639(ν_{CO}). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 24.2 (d, $^2J_{PP}$ = 44, $^2J_{PC}$ = 115 Hz, P trans to acetyl), 26 (br d, $^2J_{PP}$ = 44 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 209-212 (m, CO), 235.0 (dd, J_{PC} = 12, 115 Hz, *C*(O)CH_3).

11 Other possible mechanisms are as follows. a) Heterolytic cleavage of Pd-Co bond generates [PdMe(dpe)][Co$(CO)_4$], and CO insertion takes place on the Pd cation.[12] However, this is less probable because no retardation effect was observed when 1 equiv. of [PPN][Co$(CO)_4$][13] was added to the reaction system of **3**. b) Partial dissociation of dpe occurs to be monodentate, and the semibridging CO migrates to the fourth coordination site on Pd to result in the CO insertion. To explore this possibility, 1 equiv. of dpe or PMe_3 was added to **3**, but ionization was very facile to give ionic complexes such as [PdMe(PMe_3)(dpe)][Co$(CO)_4$]. Therefore, it was difficult to prove this mechanism. See also refs. 2d and 12a for the formation of similar cationic Pt and Pd complexes. c) ^{13}CO enhances reductive elimination of MeCo$(CO)_4$ from **3** to give "Pd(dpe)" species, and CO insertion and coordination of ^{13}CO produce AcCo$(CO)_3$(^{13}CO). Oxidative addition of the acetyl Co complex to "Pd(dpe)" gives (dpe)AcPd-Co$(CO)_3$-(^{13}CO).

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