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Oxidative Addition of Organocobalt(I) and -molybdenum(II) Complexes to Palladium(0) Complexes To Give Heterodinuclear Organometallic Complexes

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Summary: Oxidative addition of $Co(COMe)(CO)_4$ *and* $MoMeCp(CO)_3$ *to* $Pd(dba)_2$ *(dba = dibenzylideneacetone) in the presence of the bidentate ligand* L_2 *(*L_2 *= dppe (1,2-bis(diphenylphosphino)ethane), tmeda (N,N,N′,N′-tetramethylethylenediamine), bpy (2,2′-bipyridine), phen (1,10-phenanthroline)) takes place to give* $L_2(MeCO)Pd-Co(CO)_4$ *(*L_2 *= dppe (**1**), tmeda (**2**), bpy (**3**), phen (**4**)) and (dppe)MePd−MoCp(CO)*$_3$ *(**5**), respectively.*

Synergism of heterotransition metals in catalysis and materials is a challenging unsolved subject of current interest and understanding of such effects at a molecular level may offer novel basic ideas for the creation of more effective catalysts.[1] We previously prepared a series of heterodinuclear organometallic complexes having both M−M′ and M−C bonds as the simplest model compounds, $L_mRM-M'L_n$.[2] One characteristic reaction of such complexes is alkyl or hydride ligand (R) migration from M to M′ under ambient conditions to give $M'RL_n$.[2a−c,f] The reaction may be regarded as reductive elimination at M. On the other hand, the reverse of this process, oxidative addition of an organotransition metal−carbon bond to a low-valent, coordinatively unsaturated transition-metal species also is conceivable. However, such a process has not been well-established thus far,[3] although it has been postulated as a step in the mechanism of the enhanced CO insertion into heterodinuclear methylpalladium complexes.[4] On the other

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(1) (a) Chetcuti, M. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 10, pp 351−385. (b) Braunstein, P.; Rose, J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 10, pp 23−84. (c) Beringhelli, T.; Ceriotti, A.; D'Alfonso, G.; Della Pergola, R.; Ciani, G.; Moret, M.; Sironi, A. *Orgnaometallics* **1990**, *9*, 1053. (d) Knorr, M.; Strohmann, C. *Organometallics* **1999**, *18*, 248.

(2) (a) Komiya, S.; Endo, I. *Chem. Lett.* **1988**, 1709. (b) Fukuoka, A.; Sadashima, T.; Endo, I.; Ohashi, N.; Kambara, Y.; Sugiura, T.; Komiya, S. *Organometallics* **1994**, *13*, 4033. (c) Fukuoka, A.; Sadashima, T.; Sugiura, T.; Wu, X.; Mizuho, Y.; Komiya, S. *J. Organomet. Chem.* **1994**, *473*, 139. (d) Komiya, S.; Endo, I.; Fukuoka, A.; Hirano, M. *Trends Organomet. Chem.* **1994**, *1*, 223. (e) Fukuoka, A.; Sugiura, T.; Yasuda, T.; Taguchi, T.; Hirano, M.; Komiya, S. *Chem. Lett.* **1997**, 329. (f) Fukuoka, A.; Fukagawa, S.; Hirano, M.; Komiya, S. *Chem. Lett.* **1997**, 377. (g) Yasuda, T.; Fukuoka, A.; Hirano, M.; Komiya, S. *Chem. Lett.* **1998**, 29. (h) Misumi, Y.; Ishii, Y.; Hidai, M. *Chem. Lett.* **1994**, 695. (i) Misumi, Y.; Ishii, Y.; Hidai, M. *Organometallics* **1995**, *14*, 1770. (j) Misumi, Y.; Ishii, Y.; Hidai, M. *J. Chem. Soc., Dalton Trans.* **1995**, 3489.

(3) Oxidative addition of main-group-metal−carbon bonds to Pd(0) complexes has been proposed in the Pd-catalyzed C−C bond formation of alkynylstannane with aryl iodide: (a) Shirakawa, E.; Yoshida, H.; Hiyama, T. *Tetrahedron Lett.* **1997**, *38*, 5177. Oxidative additions of organostannanes to Pt(0) complexes are known: (b) Eaborn, C.; Kundu, K.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1223. (c) Butler, G.; Eaborn, C.; Pidcock, A. *J. Organomet. Chem.* **1979**, *181*, 47. (d) Butler, G.; Eaborn, C.; Pidcock, A. *J. Organomet. Chem.* **1978**, *144*, C23. (e) Eaborn, C.; Piscock, A.; Steele, B. R. *J. Chem. Soc., Dalton Trans.* **1976**, 767. (f) Cetinkaya, B.; Lappert, M. F.; McMeeking, J.; Palmer, D. E. *J. Chem. Soc., Dalton Trans.* **1973**, 1202.

(4) Theoretical calculations of the enhanced carbonyl insertion reaction into the Me−Pd bond of the MePd−Co heterodinuclear complex (dppe)MePd−$Co(CO)_4$ using B3LYP hybrid density functional theory revealed that the most favorable pathway involves methyl group migration from Pd to Co followed by CO insertion, and subsequent acetyl group migration from Co to Pd gives (dppe)(MeCO)Pd−Co-$(CO)_4$: Koga, N. Personal communication.

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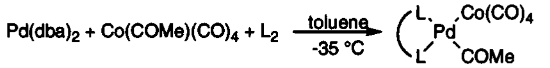
hand, oxidative addition of a M−H bond of a transition-metal hydride to another metal complex is known.[2g,5] In this paper we report the oxidative additions of the M−C σ bonds of acetylcobalt(I) and methylmolybdenum(II) complexes to zerovalent Pd, which give heterodinuclear organometallic complexes. Such reactions can also be used as a new preparative method for heterodinuclear organometallic complexes.

Treatment of the zerovalent palladium complex Pd(dba)$_2$[6] (dba = dibenzylideneacetone) with acetyltetracarbonylcobalt(I)[7] in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) in toluene at −35 °C smoothly gave (dppe)(MeCO)Pd−Co(CO)$_4$ (**1**)[2f,8] in 44% isolated yield.



(1)

L_2 =	
dppe (**1**)	44%
tmeda (**2**)	71%
bpy (**3**)	83%
phen (**4**)	92%

Similar reactions in the presence of other bidentate ligands such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda), 2,2′-bipyridine (bpy), and 1,10-phenanthroline (phen) gave the corresponding heterodinuclear acetylpalladium(II) complexes L_2(MeCO)Pd−Co(CO)$_4$ (L_2 = tmeda (**2**),[9] bpy (**3**),[10] phen (**4**)[11]) in 71, 83, and 92% yields, respectively. This facile oxidative addition of the acyl−cobalt bond to a Pd(0) species supports the mechanism of enhanced CO insertion into (dppe)(Me)Pd−Co(CO)$_4$, in which the most favorable path involves methyl group migration from Pd to Co followed by CO insertion and subsequent acetyl group migration from Co to Pd, giving (dppe)(MeCO)Pd−Co(CO)$_4$ as the final product.[3]

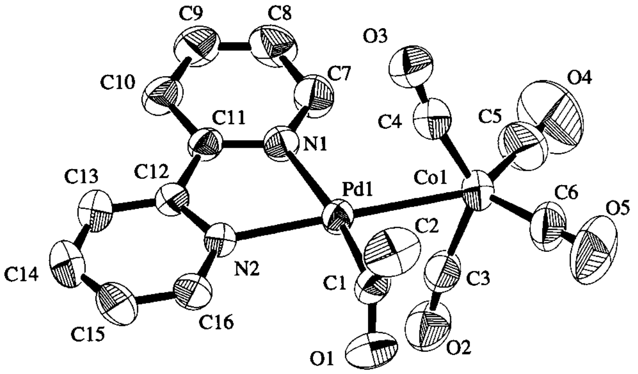
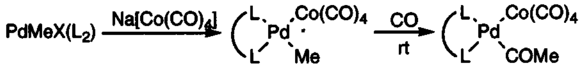


Figure 1. Molecular structure of (bpy)(MeCO)Pd−Co(CO)$_4$ (**3**). All hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability.

These complexes also were prepared by the metathetical reactions of PdMeX(L_2) (X = NO_3, Cl) with Na[Co(CO)$_4$] followed by treatment with CO (yields: **1**, 48%; **2**, 61%; **3**, 29%; **4**, 34%).



(2)

L_2 =	
dppe (**1**)	48%
tmeda (**2**)	61%
bpy (**3**)	29%
phen (**4**)	34%

These complexes **1**−**4** were characterized by ^{1}H and ^{31}P{^{1}H} NMR and IR spectroscopy and elemental analysis as well as by X-ray structure analysis. Figure 1 depicts an ORTEP drawing of one of these heterodinuclear complexes, **3**,[12] showing the presence of both Pd−Co and MeC(O)−Pd bonds. The Pd−Co distance for **3** is 2.57(2) Å, which is similar to that for (py)(PhHNN=CMeC$_6$H$_4$)Pd−Co(CO)$_4$ (py = pyridine) (2.604(1) Å)[13] but shorter than those for (Me$_3$P)$_2$(PhC(O))Pd−Co(CO)$_4$ (2.7856(7) Å)[2j] and (dppe)MePd−Co(CO)$_4$ (2.682(7) Å).[2f] The geometry at Pd is essentially square planar, where Co and the acetyl group are bonded to Pd in a cis fashion. An interesting common feature of this structure is the weak semibridging character of the carbonyl ligands. The bond angles Co(1)−C(3)−O(2) and Co(1)−C(4)−O(3) (171.9(4) and 171.3(5)°) and bond distances Pd(1)−C(3) and Pd(1)−C(4) (2.480(7) and 2.46(2) Å) are reflections of such a structure.

Oxidative addition of the R−M bond of an alkylmetal complex, MoMeCp(CO)$_3$,[14] to Pd(dba)$_2$ also took place in the presence of dppe in C$_6$D$_6$ at room temperature to give the known heterodinuclear complex (dppe)MePd−

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[5] Braunstein, P.; Faure, T.; Knorr, M.; Staehrfelt, T.; DeCian, A.; Fischer, J. *Gazz. Chim. Ital.* **1995**, *125*, 35, and references therein.

[6] Ukai, T.; Kawazura, H.; Ishii, Y.; Bennet, J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

[7] des Abbayes, H.; Buloup, A. *J. Organomet. Chem.* **1979**, *179*, C21.

[8] As a typical procedure, oxidative addition of Co(COMe)(CO)$_4$ to Pd(dba)$_2$ in the presence of dppe to afford (dppe)(MeCO)Pd−Co(CO)$_4$ (**1**) is given. To a solution of Pd(dba)$_2$ (170.5 mg, 0.2965 mmol) in toluene was added a toluene solution of Co(COMe)Co(CO)$_4$ (0.20 M, 2.0 mL, 0.40 mmol) at −35 °C, and the mixture was stirred for several minutes. To the mixture was added a solution of dppe (119.7 mg, 0.3004 mmol) in toluene at that temperature. The reaction mixture was stirred at −35 °C overnight. The reaction mixture was evaporated to dryness in vacuo, giving a red solid, which was washed with hexane. Recrystallization from benzene gave orange crystals (yield: 44%). Physical and spectroscopic data for **1** are as follows. Mp: 118 °C dec. Molar electrical conductivity Λ (THF, 24 °C): 0.18 S cm^2 mol^{-1}. Anal. Found: C, 53.47; H, 3.88. Calcd for C$_{32}$H$_{27}$O$_5$P$_2$CoPd: C, 53.47; H, 3.79. IR (KBr, cm^{-1}): 2025 s, 1951 s, 1919 s, 1680 s (ν(CO)). ^{1}H NMR (C$_6$D$_6$, room temperature, 300.4 MHz): δ 1.6−1.9 (m, 4H, dppe CH_2), 2.27 (s, 3H, C(O)CH_3), 7.0−7.6 (m, 20H, dppe *Ph*). ^{31}P{^{1}H} NMR (C$_6$D$_6$, room temperature, 121.6 MHz): δ 24.1 (d, $^2J_{PP}$ = 45 Hz), 26.0 (d, $^2J_{PP}$ = 45 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$, room temperature, 74.5 MHz): δ 25.4 (dd, J_{PC} = 23, 14 Hz, dppe CH_2), 27.3 (dd, J_{PC} = 27, 19 Hz, dppe CH_2), 39.1 (dd, J_{PC} = 42, 21 Hz, CH_3), 129−134 (m, dppe *Ph*), 209−212 (m, CO), 235.0 (dd, J_{PC} = 115, 12 Hz, C(O)CH_3).

[9] Physical and spectroscopic data for **2** are as follows. Mp: 88−90 °C dec. Molar electrical conductivity Λ (THF, 24 °C): 0.006 S cm^2 mol^{-1}. Anal. Found: C, 32.63; H, 4.77; N, 6.80. Calcd for C$_{12}$H$_{19}$CoN$_2$O$_5$Pd: C, 33.01; H, 4.39; N, 6.42. IR (KBr, cm^{-1}): 2016 s, 1943 s, 1923 s, 1891 s, 1682 s (ν(CO)). ^{1}H NMR (C$_6$D$_6$, room temperature, 300.4 MHz): δ 1.50 (br s, 4H, tmeda CH_2), 1.78 (br s, 12H, tmeda CH_3), 2.33 (s, 3H, C(O)CH_3).

[10] Physical and spectroscopic data for **3** are as follows. Mp: 140−142 °C dec. Molar electrical conductivity Λ (THF, 24 °C): 0.003 S cm^2 mol^{-1}. Anal. Found: C, 40.32; H, 2.33; N, 5.88. Calcd for C$_{16}$H$_{11}$CoN$_2$O$_5$Pd: C, 40.42; H, 2.35; N, 6.00. IR (KBr, cm^{-1}): 2025 s, 1951 s, 1925 s, 1877 s, 1683 s (ν(CO)). ^{1}H NMR (C$_6$D$_6$, room temperature, 300.4 MHz): δ 2.63 (s, 3H, C(O)CH_3), 6.31 (d, J = 8.1 Hz, 2H, bpy H5, H5′), 6.61 (d, J = 8.1 Hz, 2H, bpy H5, H5′), 6.68 (d, J = 8.1 Hz, 2H, bpy H4, H4′), 8.30 (d, J = 8.1 Hz, 2H, bpy H6, H6′).

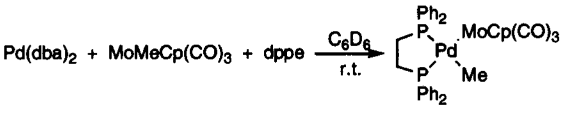
[11] Physical and spectroscopic data for **4** are as follows. Mp: 158 °C dec. Molar electrical conductivity Λ (THF, 24 °C): 0.019 S cm^2 mol^{-1}. Anal. Found: C, 43.11; H, 2.08; N, 5.61. Calcd for C$_{18}$H$_{11}$CoN$_2$O$_5$Pd: C, 43.18; H, 2.21; N, 5.60. IR (KBr, cm^{-1}): 2029 s, 1969 s, 1933 s, 1885 s, 1654 s (ν(CO)). ^{1}H NMR (acetone-d_6, room temperature, 300.4 MHz): δ 2.68 (s, 3H, C(O)CH_3), 8.16 (dd, J = 4.8, 1.2 Hz, 2H, phen H3, H8), 8.27 (s, 2H, phen H5, H6), 8.84 (dd, J = 4.8, 1.2 Hz, 2H, phen H2, H9), 8.90 (br, 2H, phen H4, H7).

[12] Crystallographic data for **3**: monoclinic, $P2_1/c$ (No. 14), a = 10.65(8) Å, b = 7.58(5) Å, c = 21.48(6) Å, β = 94.0(4)°, V = 1730(16) Å^3, Z = 4, D_{calcd} = 1.830 g cm^{-3}, T = 293 K, 4530 unique reflections, 2629 with $I > 3\sigma(I)$, R (R_w) = 0.038 (0.078).

[13] Le Borgne, G.; Bouaoud, S. E.; Grandjean, D.; Braunstein, P.; Dchand, J.; Pfeffer, M. *J. Organomet. Chem.* **1977**, *136*, 375.

[14] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

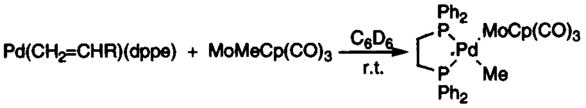
$MoCp(CO)_3$ (**5**)[2f,15] in 31% yield. The yield of **5** increased



(3)

5 (31%)

to 94 or 68% when (*n*-butyl acrylate)- or (acrylonitrile)-{1,2-bis(diphenylphosphino)ethane}palladium(0)[16] was employed as the starting Pd(0) complex. However,



(4)

5

R = CO_2Bu^n 94%

CN 68%

(maleic anhydride){1,2-bis(diphenylphosphino)ethane}palladium(0)[17] was unreactive. Facile dissociation of the olefin ligand to give reactive coordinatively unsaturated species must occur before the oxidative addition takes place. (dppe)MePd−$MoCp(CO)_3$ can also be synthesized by the metathetical reaction of $PdMe(NO_3)$(dppe) with Na[$MoCp(CO)_3$].[2f]

The present results show that oxidative addition of a transition-metal−carbon bond can take place to give heterodinuclear complexes having both M−M′ and M−C bonds, implying that the organic group transfer reaction at heterodinuclear complexes $L_mRM{-}M'L_n$ is essentially a reversible process. Such a facile R group migration process between transition metals most likely is taking place in many bimetallic catalyses.

Acknowledgment. The work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

Supporting Information Available: Tables of crystallographic data, atom coordinates, thermal parameters, and bond distances and angles for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] Physical and spectroscopic data for **5** are as follows. Mp: 122 °C dec. Molar electrical conductivity Λ (THF, 24 °C): 0.0069 S cm^2 mol^{-1}. Anal. Found: C, 55.35; H, 4.48. Calcd for $C_{35}H_{32}O_3P_2MoPd$: C, 54.96; H, 4.22. IR (KBr, cm^{-1}): 1901 s, 1792 s (ν(CO)). ^{1}H NMR (C_6D_6, room temperature, 300.4 MHz): δ 1.52 (dd, ^3J = 7.8, 6.0 Hz, 3H, Me), 1.7−1.8 (m, 4H, dppe CH_2), 4.69 (s, 5H, Cp), 7.0−7.8 (m, 20H, dppe Ph). $^{31}P\{^1H\}$ NMR (C_6D_6, room temperature, 121.6 MHz): δ 35.4 (d, $^2J_{PP}$ = 18 Hz), 56.8 (d, $^2J_{PP}$ = 18 Hz).

[16] These alkene complexes were prepared by the reaction of $PdCl_2$(dppe) with $NaBH_4$ in the presence of a large excess of the alkene according to the analogous literature method.[18]

[17] Takahashi, S.; Hagiwara. N. *Nippon Kagaku Kaishi* **1967**, *88*, 1306; *Chem. Abstr.* **1968**, *69*, 27514g.

[18] Jutand, A.; Hii, K. K.; Thornton-Pett, M.; Brown, J. M. *Organometallics* **1999**, *18*, 5367.