phosphine, δ −29.7 (d, J = 67 Hz, PHPr-*i*) and −122.6 (d, J = 67 Hz, PH_2), the trialkylated diphosphine δ −1.7 [d, J = 108 Hz, $P(Pr\text{-}i)_2$] and −23.6 (d, J = 108 Hz, PHPr-*i*), and **6b** (meso and *dl*), δ −27.6 (s) and −31.5 (s); these species were present in an estimated ratio of 1:1:10, respectively. The mixture was redistilled to give three equal fractions (0.6 g) boiling over the range 120–130 °C (5 mm). The first fraction was enriched in the monoalkylated diphosphine and the third in the trialkylated material, and the second was further enriched in **6b** (estimated ratio mono:tri:**6b** = 1:1:20): ^1H NMR ($CDCl_3$) δ 7.5 (m, 4 H), 4.2 (dm, J = 200 Hz, 2 H), 2.3 (m, 2 H), 1.2 (m, 12 H); ^{13}C NMR ($CDCl_3$) 140.6 (t, J = 5.3 Hz), 135.7 (t, J = 5.2 Hz), 128.2 (s), 24.3 (t, J = 2.8 Hz), 22.0 (t, J = 5.3 Hz). Anal. Calcd for $C_{12}H_{20}P_2$: C, 63.71; H, 8.91. Found: C, 63.85; H, 8.86.

Acknowledgment. Financial support from the National Science Foundation (Grant CHE81-13090), the Robert A. Welch Foundation (Grant F573), and the Air Force Office of Scientific Research (Grant AFOSR-79-0090).

Registry No. **3**, 15104-46-8; **4**, 15104-43-5; **5**, 80510-04-9; *meso*-**6a**, 87532-91-0; *dl*-**6a**, 87532-95-4; *meso*-**6b**, 87532-92-1; *dl*-**6b**, 87532-94-3; **7**, 7237-07-2; trimethyl phosphite, 121-45-9; 1,2-dichlorobenzene, 95-50-1; methyl iodide, 74-88-4; 2-bromopropane, 75-26-3; 1-(di-2-propylphosphino)-2-(2-porpylphosphino)benzene, 87532-93-2.

Supplementary Material Available: Additional experimental data (2 pages). Ordering information is given on any current masthead page.

Communications

Study of Group 8 Metal Promoters in the Cobalt-Catalyzed Carbonylation of Methanol to Acetaldehyde

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Summary: Transition-metal halides, $MCl_3\cdot 3H_2O$, where M = Rh, Ir, and Ru, have been found to be promoters for the cobalt-catalyzed carbonylation of methanol to acetaldehyde, and their role as promoters has been investigated. $RhCl_3\cdot 3H_2O$ is known to stoichiometrically liberate HI when reacted in the presence of LiI and carbon monoxide. This liberated acid acts as a temporary promoter for the carbonylation as a result of rapid formation of methyl iodide from methanol and HI. The same temporary promotion is observed by substituting equimolar amounts of HI for $RhCl_3\cdot 3H_2O$. Under identical reaction conditions, the addition of $IrCl_3\cdot 3H_2O$ or $RuCl_3\cdot 3H_2O$ is shown to result in a similar type of promotion.

Multimetallic catalysts are of interest due to the potential for the different metals cooperating during chemical transformations.[1] It is hoped that this cooperativity will aid in the design of new, more selective catalysts that will provide high reaction rates and operate under mild conditions. Numerous claims and reports of the use of two or more metals to catalyze various reactions have appeared in the literature.[2] However, few homogeneous, multimetallic catalysts have been substantiated.[3] We have been studying the cobalt/iodide catalyzed reductive carbonylation of methanol to acetaldehyde[4] and have found that the addition of group 8 metal salts as promoters results in an increase in the rate of reaction. We report here that this rate enhancement is not due to metal cooperativity, but it is a result of the ability of the promoting metal to generate acid in situ.

Group 8 metal salts such as $RhCl_3\cdot 3H_2O$, $IrCl_3\cdot 3H_2O$, and $RuCl_3\cdot 3H_2O$ are effective to varying degrees as cocatalysts with $Co(OAc)_2\cdot 4H_2O$/LiI for the carbonylation of methanol to acetaldehyde (Table I).[5] The observation that all of the promoting metal salts are almost equally effective

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[1] (a) Roberts, D. A.; Geoffroy, G. L. In "Comprehensive Organometallic Chemistry", 6th ed.; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 40. (b) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207. (c) Finke, R. G.; Gaughan, G.; Pierpont, C.; Cass, M. E. *J. Am. Chem. Soc.* **1981**, *103*, 1394 and references therein. (d) Breen, M. J.; Duttera, M. R.; Geoffroy, G. L.; Novotnak, G. C.; Roberts, D. A.; Shulman, P. M.; Steinmetz, G. R. *Organometallics* **1982**, *1*, 1008. (e) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2489. (f) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (g) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

[2] (a) Alemdaroglu, N. H.; Penninger, J. L. M.; Oltay, E. *Monatsh. Chem.* **1976**, *107*, 1153. (b) Demitras, G. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 2796. (c) Doyle, G. (Exxon) U. S. Patent, 4 348 541. (d) Pruett, R. L.; Bradley, J. S. (Exxon) U.S. Patent 4 342 838. (e) Doyle, G. (Exxon) U.S. Patent 4 320 230. (f) Korff, J.; Fremery, M.; Zimmerman, J. (Union Rheinische) U.S. Patent 4 278 987. (g) Cornils, B. In "New Syntheses with Carbon Monoxide"; Falbe, J., Ed.; Springer-Verlag: New York, 1980; p 44 and references therein. (h) Fiato, R. A. (Union Carbide) U.S. Patent 4 253 987. (i) Ungermann, C.; Landis, V.; Moya, S. A.; Cohen, H.; Walker, H.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 5922. (j) Knifton, J. F. (Texaco) U.S. Patent 4 332 914. (k) Hidai, M.; Orisaka, M.; Ue, M.; Koyasu, Y.; Kodama, T.; Uchida, Y. *Organometallics* **1983**, *2*, 292. (l) Muetterties, E. L.; Krause, M. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 135.

[3] The Wacker Process for the carbonylation of ethylene to acetaldehyde uses a palladium/copper bimetallic catalyst. There is strong evidence that the cobalt-catalyzed hydroformylation is bimetallic.[2a] The cobalt/iodide and various cobalt/ruthenium/iodide based catalysts for the carbonylation of methanol to acetaldehyde or ethanol are examples where bimetallic cobalt catalysis as in hydroformylation is observed. However, the role of ruthenium in the latter is only to catalyze the reduction of acetaldehyde to ethanol and does not interact in a cooperative manner with cobalt in any key reaction step.[18]

[4] (a) Berty, J.; Marko, L. *Chem. Tech.* (*Leipzig*) **1956**, *8*, 260. (b) Fakley, M. E. Head, R. A. *Appl. Catal.* **1983**, *5*, 3.

[5] The reactants are loaded into a 300-mL Hastelloy C autoclave designed to operate in a rocking mode. The autoclave is pressurized with 100 psig of 1/1 CO/H_2 at room temperature and vented. The autoclave is repressurized to 100 psig, sealed, heated, and rocked until the desired reaction temperature is reached. Then additional CO/H_2 gas mixture is added until the desired pressure is reached. The time at which the desired autoclave internal pressure is reached is taken as T_0. Reactor pressure is maintained at the preset value during the experiment by adding the CO/H_2 gas mixture from a surge tank. When the predetermined reaction time is complete, the autoclave is rapidly cooled by a stream of cold air. After the gas is vented from the autoclave, the reaction product is analyzed by gas chromatographic methods with a POROPAK Q column with an acetonitrile internal standard.

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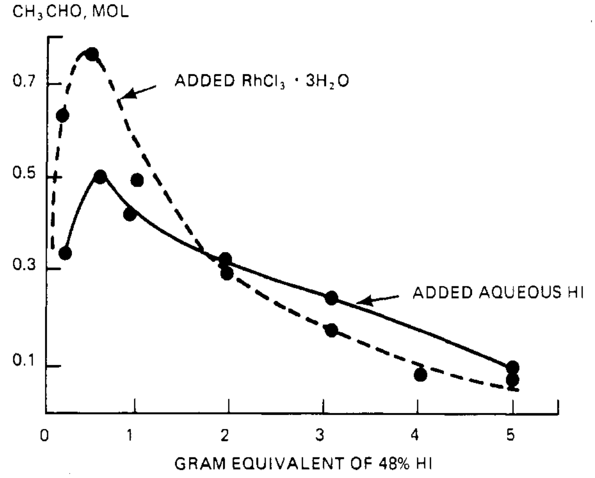

Figure 1. Comparison of the effect of the addition of 48% aqueous HI and $RhCl_3{\cdot}3H_2O$ as promoters on acetaldehyde formation.

prompted further investigation of this enhancement effect. The addition of 0.5 equiv or less of $RhCl_3{\cdot}3H_2O$ to a $Co(OAc)_2{\cdot}4H_2O/LiI$ catalyst mixture causes the initial production rate of acetaldehyde to approximately double as compared to that of the unpromoted cobalt/lithium iodide catalyst (Table I).[6] Infrared examination of a typical reaction solution shows two characteristic carbonyl bands at 2060 (s) and 1990 (s) cm^{-1} attributed to the presence of $[Rh(CO)_2I_2]^-$ and one at 1900 (s) cm^{-1} attributed to $[Co(CO)_4]^-$ (eq 1). Addition of Bu_4NI to the reaction solution results in the isolation of $[Bu_4N][Rh(CO)_2I_2]$ in a 93% yield.[7]

$$Co(OAc)_2{\cdot}4H_2O + LiI + RhCl_3{\cdot}3H_2O \xrightarrow[CO/H_2]{MeOH} Li[Co(CO)_4] + Li[Rh(CO)_2I_2] \quad (1)$$

The reaction of $RhX_3{\cdot}H_2O$ with water and carbon monoxide is known to give $[Rh(CO)_2X_2]^-$, where X = Cl, Br, or I, and 2 equiv of acid (eq 2).[8] To test the effect of

$$RhX_3 + H_2O + CO \rightarrow [Rh(CO)_2X_2]^- + CO_2 + 2H^+ \quad (2)$$

acid on the yield of acetaldehyde, a series of $Co(OAc)_2{\cdot}4H_2O/LiI$ catalyzed carbonylations have been conducted with varying amounts of aqueous HI (Table I, Figure 1).[9,10] It is readily evident from Figure 1 that the amount of acetaldehyde formed is dependent on the HI concentration. In another series of experiments, varying the amount of $RhCl_3{\cdot}3H_2O$ results in an acetaldehyde dependence on $RhCl_3{\cdot}3H_2O$ concentration similar to that observed for the addition of HI (Table I, Figure 1).[11] Therefore, it appears

Table I. Effect of Catalyst Composition on Carbonylation of Methanol to Acetaldehyde[a]

catalysts, g					liquid product,[b] mol							
$Co(OAc)_2{\cdot}4H_2O$	$RhCl_3{\cdot}3H_2O$	LiI	48% HI	other	H_2O	MeOH	AcH[c]	MeI	MeOAc	EtOH	EtOAc	HOAc
0.50		9.0			1.43	2.43	0.30	0.010	0.07		0.014	0.014
0.50	0.25	9.0			1.78	1.96	0.75	0.010	0.11	0.009	0.029	
0.50		9.0		0.25 $RuCl_3{\cdot}3H_2O$	1.62	1.94	0.50	0.007	0.12	0.17	0.003	0.023
0.50		9.0		0.25 $IrCl_3{\cdot}3H_2O$	1.81	1.73	0.69	0.009	0.15	0.077	0.009	0.050
0.50		9.0	0.25		1.96	1.23	0.32	0.013	0.07		0.002	0.021
0.50		9.0	0.50		1.75	1.97	0.50	0.015	0.11		0.008	0.020
0.50		9.0	1.00		1.74	1.78	0.42	0.007	0.10		0.004	0.009
0.50		9.0	2.00		1.62	1.48	0.33	0.016	0.07		0.001	0.008
0.50		9.0	3.00		1.76	1.22	0.26	0.010	0.06			
0.50		9.0	5.00		1.84	0.91	0.12	0.007	0.06			0.034
0.50	0.125	9.0			1.67	1.84	0.66	0.035	0.10	0.020	0.021	
0.50	0.25	9.0			1.78	1.96	0.75	0.010	0.11	0.009	0.029	
0.50	0.50	9.0			1.61	1.90	0.47	0.011	0.10		0.005	
0.50	1.00	9.0			1.45	1.98	0.29	0.011	0.08			
0.50	1.50	9.0			1.77	1.75	0.14	0.018	0.14			0.039
0.50	2.00	9.0			1.83	1.41	0.09	0.015	0.08			0.016
0.50	2.50	9.0			2.21	1.93	0.09	0.014	0.08		0.001	

[a] Reaction conditions: 4000 psig; 1/1 CO/H_2; 195 °C; 0.5 h reaction time; 3 mol of methanol; 1 mol of H_2O. [b] Dimethyl ether was not measured. [c] Total acetaldehyde plus dimethyl acetal.

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(6) Apparently, $[Rh(CO)_2I_2]^-$ does not compete with $[Co(CO)_4]^-$ for the methyl iodide because acetic acid is the minor product. However, at higher methyl iodide concentrations, cobalt carbonyl complexes are destabilized to Co^{2+} salts, and $[Rh(CO)_2I_2]^-$ catalyzes the carbonylation of methyl iodide to give almost exclusively acetic acid.

(7) The $[Co(CO)_4]^-$ was not isolated. Anal. Calcd for $C_{18}H_{36}NO_2I_2Rh$: C, 33.00; H, 5.54. Found: C, 33.12; H, 5.72. IR (THF): 2051 (s) and 1985 (s) cm^{-1}.

(8) James, B. R.; Rempel, G. L. *Chem. Commun.* **1967**, 158.

(9) (a) The HI curve can be duplicated by addition of methyl iodide instead of HI. (b) The small deviation in acetaldehyde concentration (Figure 1) observed at low values of added $RhCl_3{\cdot}3H_2O$ when compared to HI appears to be due to the difference between aqueous HI being initially added to the autoclave vs. HI being generated in situ from $RhCl_3{\cdot}3H_2O$.

(10) Similar effects with methyl iodide and HI have been observed: Mizoroki, T.; Nakayama, M. *Bull. Soc. Chem. Jpn.* **1968**, *41*, 1628.

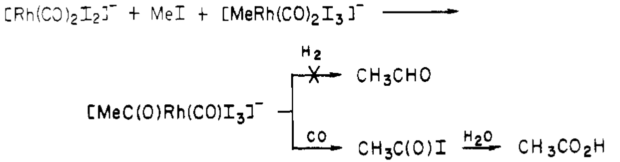
(11) The added $RhCl_3{\cdot}3H_2O$ reflects 2 equiv of acid liberated under reaction conditions. For example, 0.25 g (9.5×10^{-4} mol) $RhCl_3{\cdot}3H_2O$ should liberate 1.9×10^{-3} mol of HI which is equivalent to 0.50 g of 48% aqueous HI.

that the promotional effect of added $RhCl_3{\cdot}3H_2O$ is only a consequence of in situ production of HI.

It is not surprising to find that the amount of HI affects the reaction. It is known that HI reacts rapidly with methanol to give methyl iodide (eq 3) which can subsequently react with either $[Co(CO)_4]^-$ (eq 4) or $[Rh(CO)_2I_2]^-$ (eq 5).[12,13] Only cobalt, however, is known to catalyze the production of acetaldehyde.

$$HI + MeOH \rightleftharpoons H_2O + MeI \quad (3)$$

$$[Co(CO)_4]^- + MeI \rightarrow MeCo(CO)_4 + I^- \xrightarrow{CO} MeC(=O)Co(CO)_4 \xrightarrow{[H]} CH_3CHO \quad (4)$$



$$[Rh(CO)_2I_2]^- + MeI + [MeRh(CO)_2I_3]^- \longrightarrow [MeC(O)Rh(CO)I_3]^- \begin{cases} \overset{H_2}{\nrightarrow} CH_3CHO \\ \xrightarrow{CO} CH_3C(O)I \xrightarrow{H_2O} CH_3CO_2H \end{cases} \quad (5)$$

Iodide promoters are beneficial but are not necessary. Methanol will react with $HCo(CO)_4$ under reaction conditions of high temperature and pressure but at much lower rates than in promoted systems. The probable reason for the iodide enhancement is that water is a much poorer leaving group than iodide (eq 6).[14]

$$CH_3OH + H^+ \rightarrow CH_3OH_2^+ \xrightarrow{[Co(CO)_4]^-} CH_3Co(CO)_4 + H_2O \quad (6)$$

Transformations similar to the one shown in eq 2 are not limited to rhodium. Both promoted and unpromoted cobalt catalysts generate their own acid via the reduction of Co(II) to Co(I−) (eq 7).[15,18]

$$2Co^{2+} \overset{H_2/CO}{\rightleftharpoons} Co_2(CO)_8 + 4H^+ \overset{H_2}{\rightleftharpoons} 2HCo(CO)_4 \rightleftharpoons 2H^+ + 2[Co(CO)_4]^- \quad (7)$$

As shown in Figure 2 where the reaction was conducted at 160 °C, the differences in acetaldehyde yields among rhodium and HI-promoted and -unpromoted catalysts are small after 0.5 h.[16] The differences in acetaldehyde yield observed at 0.5 h between the various catalysts are reproducible just as they are at 195 °C. However, the differences become less discernible and the ability to reproduce small differences in yield becomes more difficult as the reaction proceeds. Nevertheless, if rhodium contributed in a manner other than the stoichiometric generation of acid, differences in product yield or selectively comparable or greater than the initial observable differences should be observed at the longer reaction times. Since no large differences are apparent at longer reaction times, it appears that the sole function of $RhCl_3{\cdot}3H_2O$ is the stoichiometric generation of acid which quickly establishes equilibrium conditions necessary for a rapid reaction rate. Apparently unpromoted cobalt is slower in approaching equilibrium.

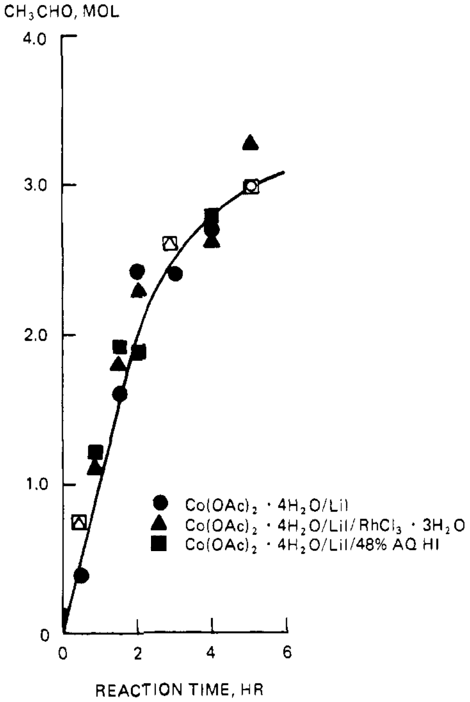


Figure 2. Effect of longer reaction times on the acetaldehyde yield with promoted and unpromoted cobalt catalysts.[16] Reaction conditions: 4000 psig; 1/1 CO/H_2; 160 °C; 15 mol of methanol; 5 mol of H_2O.

At short reaction times, the nonequilibrium conditions are apparently responsible for the observed rate enhancement. Once equilibrium has been established, any initial difference becomes less significant at longer reaction times. Note that the addition of excess HI results in decreased yields of acetaldehyde; this decrease is related to the instability of $Co_2(CO)_8$ in acidic solutions (eq 7).[15b] HI is needed for the formation of methyl iodide, but excess acid results in the decarbonylation of $Co_2(CO)_8$ to Co^{2+}. Clearly there is an optimum concentration of acid that maximizes the rate of carbonylation of methanol without causing excessive decarbonylation of $Co_2(CO)_8$.

Both $RuCl_3{\cdot}3H_2O$ and $IrCl_3{\cdot}3H_2O$ are thought to be acid formers although these metals are slightly less active than $RhCl_3{\cdot}3H_2O$ as promoters (Table I).[17,18] Infrared spectral analysis of reaction solutions that contained $RuCl_3{\cdot}3H_2O$ as a promoter show characteristic carbonyl bands at 2100 (s) and 2024 (s) cm^{-1} from $[Ru(CO)_3I_3]^-$ and one band at 1900 (s) cm^{-1} from $[Co(CO)_4]^-$. Upon workup of reaction solutions that contain $IrCl_3{\cdot}3H_2O$ as a promoter, $Ir_4(CO)_{12}$ is isolated as an insoluble yellow precipitate, and a carbonyl band at 1900 cm^{-1} is observed in the infrared spectrum from $[Co(CO)_4]^-$.[19]

It has been shown that the observed acetaldehyde rate enhancement is not due to metal cooperativity but is a result of the ability of the promoting metal to generate acid in situ. Additionally, this study shows some of the dangers of interpreting the results of single-analysis, batch autoclave experiments that are the basis of many patents. The

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(12) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1962**, *84*, 2499.

(13) Forster, D. *J. Am. Chem. Soc.* **1976**, 98, 846.

(14) Wender, I.; Levine, R.; Orchin, M. *J. Am. Chem. Soc.* **1949**, *71*, 4160.

(15) (a) Alemdaroglu, N. H.; Penninger, J. M. L.; Oltay, E. *Monatsh. Chem.* **1976**, *107*, 1043. (b) Usami, S.; Nishimura K.; Koyama, S.; Fukushi, S. (Toa Nenryo) U.S. Patent 3634291.

(16) (a) These carbonylation experiments are done similarly[5] except in a stirred 1800-mL Hastelloy B autoclave with samples taken at predetermined intervals from a sample tube. (b) High concentrations of water formed from the conversion of methanol to methyl iodide inhibit acetaldehyde formation at longer reaction times. (c) The lower temperature is used to keep conversions low. (d) Although not shown, the selectivity differences are also minimal.

(17) The reduction of ruthenium and iridium salts to $Ir_4(CO)_{12}$ and $Ru_3(CO)_{12}$ is thought to proceed through metal halocarbonyl complexes similar to that of rhodium. (a) Whyman R. *J. Chem. Soc., Dalton Trans.* **1972**, 2294. (b) Montovani, A.; Cenini, S. *Inorg. Synth.* **1976**, *16*, 47.

(18) Although ruthenium can reduce acetaldehyde to ethanol under these conditions (unpublished results), it has not been found to promote the carbonylation of methanol to acetaldehyde.

(19) Anal. Calcd for $C_{12}O_{12}Ir_4$: C, 13.24; H, 0.00. Found: C, 13.54; H, 0.29. Ir (KBr): 2087 (s), 2060 (vs), 2020 (m) cm^{-1}. EI mass spectrum (70 eV): *m/e* (Ir^{193}) 1108, 1080, 1052, 1024, 996, 968, 940, 912.

literature contains references to many questionable multimetallic catalysts; each of these catalysts should be viewed with skepticism unless further substantiated.[20]

Acknowledgment. We thank Dr. D. M. Pond and Dr. S. W. Polichnowski for valuable discussions.

Registry No. $RhCl_3$, 10049-07-7; $IrCl_3$, 10025-83-9; $RuCl_3$, 10049-08-8; LiI, 10377-51-2; CO, 630-08-0; MeOH, 67-56-1; CH_3CHO, 75-07-0; HI, 10034-85-2; $Co(OAc)_2$, 71-48-7; $HCo(CO)_4$, 16842-03-8; $[Co(CO)_4]^-$, 14971-27-8; $[Rh(CO)_2I_2]^-$, 38255-39-9; $[Bu_4N][Rh(CO)_2I_2]$, 13927-74-7; $Ir_4(CO)_{12}$, 11065-24-0.

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[20] A selective cobalt/nickel/PPh_3/HI catalyst for the reductive carbonylation of methanol to acetaldehyde has recently been reported.[2f] Although the claim catalyst performs well at the short reaction times illustrated in the patent, we have found that the reaction rate and selectivity decrease rapidly at longer reaction times. It appears that this chemistry is similar to that reported in this communication.

Oxidation of Organoplatinum(II) Halides with Halogens or Copper(II) Halides. Syntheses and the Molecular Structure of $[Pt^{IV}Cl_3(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$

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Summary: Stable organometallic platinum(IV) complexes $[PtX_3(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (X = Cl, Br, or I) are formed nearly quantitatively in the reaction of the square-planar platinum(II) complexes $[PtX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ with either X_2 (X = Cl, Br, or I) or $Cu^{II}X_2$ (X = Cl, Br). Products originating from Pt–C bond cleavage were not found. The structure of $[PtCl_3(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ was determined by X-ray methods.

The understanding of transmetalation reactions in terms of discrete steps improved greatly when the possible occurrence of electron-transfer reactions was taken into account. We,[1] and others,[2] showed that reactions between transition-metal d^8 complexes and post-transition-metal d^{10} salts can lead to the formation of stable dinuclear M–M′ species as well as to products originating from this species by subsequent ligand transfer or ligand exchange reactions. The latter reactions may be accompanied by electron transfer.

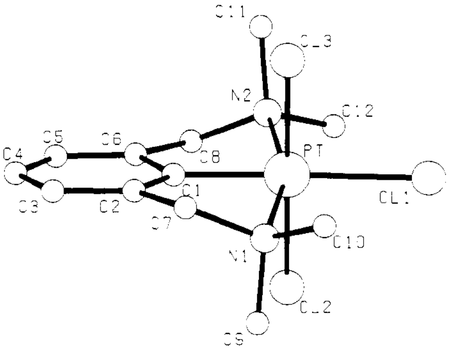


Figure 1. A PLUTO drawing of $[PtCl_3(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$, **2a**.

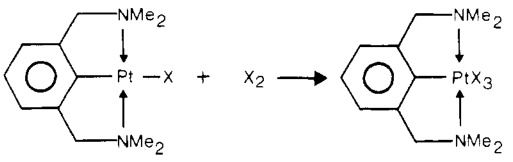
Table I. Selected Bond Lengths (Å) and Angles (deg) for 2a[a]

Bond Lengths			
Pt-C(1)	1.96 (3)	Pt-Cl(3)	2.334 (5)
Pt-Cl(1)	2.454 (8)	Pt-N(1)	2.15 (2)
Pt-Cl(2)	2.330 (5)	Pt-N(2)	2.16 (2)
Bond Angles			
N(1)-Pt-N(2)	160.7 (6)	Cl(2)-Pt-Cl(1)	89.9 (2)
Cl(1)-Pt-C(1)	178.4 (6)	Cl(3)-Pt-C(1)	91.5 (6)
Cl(2)-Pt-Cl(3)	178.6 (2)	Cl(3)-Pt-Cl(1)	89.9 (2)
Cl(2)-Pt-C(1)	88.9 (6)		

[a] Estimated esd's in parentheses.

We are further extending these studies by using the terdentate anionic ligand $o,o'\text{-}(Me_2NCH_2)_2C_6H_3$, which when bonded to a metal produces a rigid stereochemistry in which two hard nitrogen donor atoms are mutually trans across the metal center. Here we report reactions of square-planar $[Pt^{II}X(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (**1**) with the reagents X_2 and CuX_2, which are not only good electrophiles but are also known to undergo one-electron-transfer reactions.

The reactions of **1** with X_2 afford the new platinum(IV) complexes $[PtX_3(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (**2**) as summarized in eq 1 via oxidative addition. Complexes **2a** and **2b** are also obtainable from the ligand transfer oxidation reaction using $CuCl_2$ and $CuBr_2$ (eq 2) in an 1/2 molar ratio. The air-stable solid complexes **2a–c** are orange, red-brown, and dark violet, respectively.[3]



(1)

1a = Cl
1b = Br
1c = I

2a = Cl
2b = Br
2c = I

$$[Pt^{II}X(C_6H_3(CH_2NMe_2)_2\text{-}o,o')] + 2Cu^{II}X_2 \rightarrow [Pt^{IV}X_3(C_6H_3(CH_2NMe_2)_2\text{-}o,o')] + 2Cu^{I}X \quad (2)$$

Evidence for rigid donor atom coordination for the platinum(IV) complexes comes from the ^1H NMR patterns of the CH_2 and NMe_2 groups which show sharp ^{195}Pt ($I = {}^1/_2$, 34% abundance) satellites of magnitude 29–32 Hz. These values are much lower than for the platinum(II) complexes **1a–c**, which fall in the range 38–40 Hz.[4] To definitively establish the nature of these complexes an X-ray crystallographic study has been carried out on **2a**.

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[2] (a) Jawad, J. K.; Puddephatt, R. J. *Inorg. Chim. Acta* **1978**, *31*, L391. (b) McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 1240.

[3] The syntheses and characterization as well as a discussion of the mechanistic aspects of these and related complexes (containing X = alkyl or aryl) will be the subject of a forthcoming publication.

[4] The ratio of $|^3J(PtH)|$ for $[PtX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ and $[PtX_3(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ is 0.76; this ratio is typical: cf. Ruddick, J. D.; Shaw, B. L. *J. Chem. Soc.* **1969**, 2801.

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