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.

(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.

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.

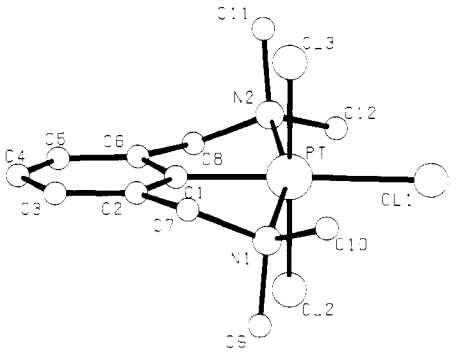


Figure 1. A PLUTO drawing of $[PtCl_3(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$, **2a**.

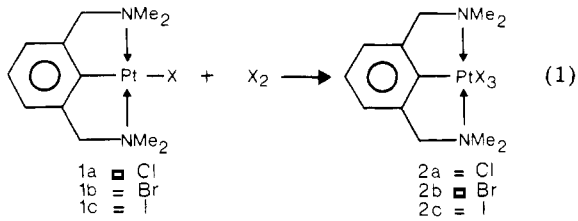
Table I. Selected Bond Lengths (Å) and Angles (deg) for **2a**[a]

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.

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**



(1)

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]

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

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**.

(1) (a) Kuijper, J. *Inorg. Chem.* **1978**, *17*, 1458. (b) van Vliet, P. J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1980**, *188*, 301. (c) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014. (d) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L.; Duisenberg, A. J. M. *Organometallics* **1982**, *1*, 1066. (e) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *Inorg. Chem.* **1982**, *21*, 2026.

(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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Crystals of the title compound are monoclinic with space group *Pn* and cell constants a = 13.760 (2) Å, b = 7.950 (2) Å, c = 7.245 (2) Å, β = 103.20 (4)°, V = 772 (2) Å^3, Z = 2, D(calcd) = 2.122 g cm^{-3}, and F(000) = 468 electrons. From the total of 2232 reflections, measured on an Enraf-Nonius CAD 4 diffractometer using graphite-monochromated Mo Kα radiation, 182 were less than 2.5$\sigma(I)$ and were treated as unobserved. No absorption correction was applied. Refinement proceeded by anisotropic block diagonal least-squares calculations resulting in a final R value of 0.039.[5]

In Figure 1 is shown the molecular geometry of the complex along with the adopted numbering scheme. Some relevant bond lengths and bond angles are given in Table I. The platinum center has a distorted octahedral geometry having a *mer* coordination of the *o,o'*-$(Me_2NCH_2)_2C_6H_3$ ligand *via* C(1) [1.96 (3) Å] and the two mutually trans positioned NMe_2 groups.[6] The principal distortion of the octahedral geometry results from the N(1)–Pt–N(2) angle of 160.7 (6)°, which is due to the intrinsically small N–Pt–C(1) bite angles of the two five-membered chelate rings. There is a significant difference in Pt–Cl bond lengths between the axial Cl atoms [2.330 (5) and 2.334 (5) Å] and meridial Cl atom [2.454 (8) Å] that points to a strong trans effect of the carbon ligand:[7] IR and Raman spectra show ν(Pt–Cl) at 260, 330, and 333 cm^{-1}.

The formation of the platinum(IV) complexes **2a** and **2b**, using the copper(II) reagents, is the result of an overall two-electron ligand transfer oxidation[8] which is preferred to Pt–C bond cleavage. It is noteworthy that the analogous reaction of $[Ni^{II}X(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ with CuX_2 stops at the stage of stable $[Ni^{III}X_2(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$, having a square-pyramidal structure.[9] These reactions can be envisaged as one-electron ligand transfer oxidations possibly involving transient formation of a M^{II}–Cu^{II} heterobimetallic intermediate (cf. $[PtAgX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(\mu\text{-}\{RNC(H)NR\})]$ (R = *p*-tolyl). In the platinum reaction a subsequent one-electron tranfer and bonding of a third halogen occurs, thus completing an octahedral geometry. This provides evidence that the constraints of the terdentate ligand can not be the factor responsible for preventing further oxidation in the corresponding nickel reactions. Further studies on the properties of these novel platinum(IV) species as well as the reactions of $[M^{II}X(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ species (M^{II} = Ni, Pd, or Pt) with oxidizing reagents are in progress.

Acknowledgment. Thanks are due to Prof. K. Vrieze for helpful discussions and to Dr. D. M. Grove for critically reading the manuscript.

Registry No. **1a**, 82112-96-7; **1b**, 67507-09-9; **1c**, 83311-96-0; **2a**, 87555-29-1; **2b**, 87555-30-4; **2c**, 87555-31-5.

Supplementary Material Available: Atomic coordinates, anisotropic thermal parameters, and interatomic distances and bond angles (3 pages). Ordering information is given on any current masthead page.

(5) The position of Pt was derived from a Patterson synthesis. The other non-hydrogen atoms were found from a subsequent ΔF synthesis.

(6) With the related ligand *o,o'*-(t-$Bu_2PCH_2)_2C_6H_3$ hexacoordinate Pt(IV) complexes so far has not been made, but indications were obtained that octahedral $[IrHCl(CO)(C_6H_3(CH_2PBu\text{-}t_2)_2\text{-}o,o')]$ exists. Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.

(7) A review covering this subject is: Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 423.

(8) Reaction of equimolar amounts of 1 and CuX_2 affords a 1/1 mixture of 2 and unreacted 1. The 1/2 reaction of $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(\mu\text{-}\{RNC(H)NR\})]$ (R = *p*-tolyl) (cf. ref. 1d) with CuX_2 afforded **2a** (or **2b**), Cu^IX, and $Cu^I(RNC(H)NR)$ (R = *p*-tolyl).

(9) Grove, D. M.; van Koten, G.; Zoet, R. *J. Am. Chem. Soc.* **1983**, *105*, 1379.

Cobalt Carbonyl Catalyzed Reaction of Tetrahydrofurans with a Hydrosilane and Carbon Monoxide at Atmospheric Pressure

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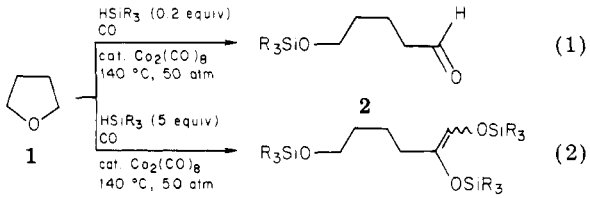
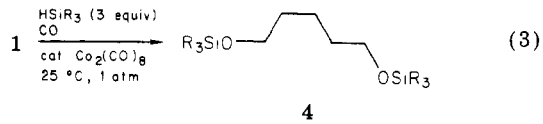
Summary: The reaction of various tetrahydrofurans with $HSiR_3$ (3 equiv) and CO (1 atm) at 25–40 °C in the presence of $Co_2(CO)_8$ (0.08 equiv) gave the corresponding diol disilyl ethers with incorporation of CO in 56–94% yield. The catalytic reaction begins with the ring opening of tetrahydrofurans with a key catalyst species, $R_3SiCo(CO)_4$, to give tetracarbonylalkylcobalt.

We have reported a series of new $Co_2(CO)_8$-catalyzed reactions with a hydrosilane ($HSiR_3$) and carbon monoxide,[1] by which incorporation of carbon monoxide into olefins,[2] aldehydes,[3,4] cyclic ethers,[4,5] and alkyl acetates[6] has been achieved. Interestingly, when tetrahydrofuran (THF), a five-membered cyclic ether, was employed as substrate, two types of products were obtained, both selectively by simply changing the molar ratio of the substrate to the hydrosilane $HSiEt_2Me$ (eq 1 and 2).[4,5] These reactions generally proceeded under *50 atm* of carbon monoxide and at *140 °C*.



R_3Si = $MeEt_2Si$

In our efforts to clarify the basic features of these reactions, we have now found another type of $Co_2(CO)_8$-catalyzed reaction of THF with a hydrosilane and carbon monoxide that gives neither **2** nor **3** but a homologated diol derivative **4**[7] (eq 3). More remarkable is that the catalytic incorporation of carbon monoxide proceeds at *atmospheric pressure* and at *room temperature*. To our knowledge, only a few cases have been recorded of a catalytic reaction of carbon monoxide at 1 atm with the aid of a cobalt catalyst.[8]



(1) For a review, see: Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837.

(2) (a) Seki, Y.; Hidaka, A.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 174. (b) Seki, Y.; Hidaka, A.; Makino, S.; Sonoda, N. *J. Organomet. Chem.* **1977**, *140*, 361.

(3) Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 393.

(4) Seki, Y.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 119.

(5) Seki, Y.; Murai, S.; Yamamoto, I.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 789.

(6) Chatani, N.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 1370.

(7) All new compounds have been adequately characterized by spectral data and elementary analyses. Details are given in the supplementary material.

0276-7333/83/2302-1883$01.50/0