ductivity at higher AsF_5 pressures has not been determined. We believe that this conductivity may be of a novel type involving loss of an electron from Si–Si bonding orbitals and delocalization of the cation radical (=hole) through the σ system.[15]

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Soluble Copper Hydrides: Solution Behavior and Reactions Related to CO Hydrogenation

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Recent mechanistic studies of synthesis gas ($CO + H_2$) reactions of the early transition elements have led to the consensus that such reactions are thermodynamically driven by the formation of strong metal–oxygen bonds.[1–5] Since such bonds appear to resist reduction by either H_2 or CO, these studies remain stoichiometric, not catalytic. We have in the past[6] and are continuing at present to move later in the transition series in search of information on reactivity trends of metals more relevant to commercial synthesis gas catalysts. Essentially all of the methanol produced industrially results from the heterogeneously catalyzed hydrogenation of carbon monoxide, much of it with a "low pressure" catalyst composed of copper and zinc oxides.[7] Motivated by this fact, the carbonyl chemistry of Cu(I) has undergone substantial recent development in the hands of Floriani and his associates.[8] In addition, a comprehensive study of a heterogeneous Cu/Zn methanol catalyst led to the conclusion that it functions by CO activation on Cu(I) and hydrogen activation on Zn(II).[9,10] Nevertheless, "activation" of H_2 may well be the more critical act than activation of CO (consider the great variety of transition-metal hydride complexes, from acidic to "hydridic"), and yet we know nothing about the spectroscopic, structural, and reactivity characteristics of copper hydrides.[11] We have therefore begun to explore the chemistry of carbonyl and hydride complexes of both Cu(I) and Zn(II).

Hydrocarbon-soluble copper/hydride/phosphine complexes were synthesized by the procedure in reaction 1, which is based on the original procedure of the Osborn group.[12] The latter showed that $x = 6$ for $R = C_6H_5$ by means of an X-ray diffraction study. The Cu_6P_6 portion of the hexamer is mildly distorted from regular octahedral symmetry by shrinkage of 6 of the 12 Cu–Cu distances. The hydrides were not detected by X-ray[12] or NMR[11,12] methods, and their existence and number was based on quantitative gas evolution studies upon acidolysis.[11,12] Our examination of the ^1H NMR spectrum (220 MHz) of $[HCuP(tol)_3]_n$ revealed (in addition to C_7H_7 resonances) a broad but structured multiplet centered on δ +3.50 in C_6D_6. Addition of CCl_4 to this solution causes the δ 3.5 resonance to disappear as $CHCl_3$ grows in,[13] and a white solid, identified as $[CuClP(tol)_3]_4$, precipitates. Under conditions of higher radio frequency power, the signal-to-noise ratio on the δ 3.5 multiplet is improved to the point where at least five components of a septet are resolved.[14a] Phosphorus decoupling of the 220-MHz ^1H NMR spectrum collapses the hydride multiplet to a singlet, thereby excluding Cu as the source of this multiplet structure. These results establish $(HCuP(tol)_3)_6$ as intramolecularly fluxional (presumably by hydride migration) and also show that the hydride chemical shift of the d^{10} species returns to the "normal" chemical shift region in comparison to the negative δ values found for complexes with partially filled d shells. Zirconium(IV)[1] and W(VI)[15] hydrides (both d^0) and also Zn(II) (see below) hydrides have chemical shifts downfield of Me_4Si.

$$(1/4)(ClCuPR_3)_4 + LiEt_3BH \rightarrow (1/x)(HCuPR_3)_x + LiCl + BEt_3 \quad (1)$$

$$R = C_6H_5,\ p\text{-}MeC_6H_4\ (\text{"tol"}),\ O\text{-}i\text{-}Pr$$

$(HCuP(tol)_3)_6$ is not hydrolyzed by excess methanol in benzene in 24 h. The ^1H NMR spectrum of a C_6D_6 solution of this complex in the presence of equimolar $P(tol)_3$ is the superposition of the spectra of the two components (the ring protons of free and coordinated phosphine are readily resolved); the hydride resonance maintains its line width and multiplicity. This establishes that phosphine exchange (and thus phosphine dissociation from the hexamer) is slow on the ^1H NMR time scale *and* that, under these conditions, the hexamer is resistant to phosphine attack and fragmentation into $[HCu(PR_3)_2]_x$ clusters or monomers;[14b] the halo clusters $(CuClPR_3)_4$ are known to fragment under these conditions.

We have examined the reaction of $(HCuP)_6$ $[P \equiv P(tol)_3]$ with formaldehyde as a representative of an intermediate carbon oxidation level on the path of CO hydrogenation.[16] Using either gaseous formaldehyde monomer or polymeric paraformaldehyde, $(HCuP)_6$ catalyzes the conversion of the aldehyde to methyl formate[17] in benzene at 25 °C. This reaction[18] (reaction 2), a

$$2H_2CO \xrightarrow{(HCuP)_6} HC(=O)OCH_3 \quad (2)$$

disproportionation of aldehyde to the alcohol and carboxylate oxidation levels, is known as the Tishchenko reaction when it is catalyzed by main group or transition-metal alkoxides.[19] This suggests that the initial reaction of $(HCuP)_6$ with formaldehyde might be reduction of the latter to a copper methoxide (reaction 3). Consistent with this is the observation (by ^2H NMR spec-

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(1) Manriquez, J. M.; McAlister, D.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716.

(2) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1976**, *230*.

(3) Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829.

(4) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

(5) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 1747.

(6) Adams, M. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1979**, *164*, C29.

(7) Kung, H. L. *Catal. Rev.* **1980**, *22*, 235.

(8) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Guastini, C. *J. Am. Chem. Soc.* **1981**, *103*, 185 and references therein.

(9) Herman, R. G.; Klier, K.; Simmons, G. W.; Finn, B. P.; Bulko, J. B.; Kobylinski, T. P. *J. Catal.* **1979**, *56*, 407.

(10) Mehta, S.; Simmons, G. W.; Klier, K.; Herman, R. G. *J. Catal.* **1979**, *57*, 339.

(11) Whitesides, G. M.; San Filippo, J.; Stedronsky, E. R.; Casey, C. P. *J. Am. Chem. Soc.* **1969**, *91*, 6542. This contains some preliminary observations on a synthetic procedure, but no spectral data.

(12) Churchill, M. R.; Bezman, S. A.; Osborn, J. A.; Wormald, J. *Inorg. Chem.* **1972**, *11*, 1818.

(13) Production of chloroform is not quantitative, and some gas evolution is observed. No copper metal is detected.

(14) (a) ^{31}P NMR spectroscopy must be employed with caution in the characterization of these clusters since the chemical shift of $(HCuP)_6$ differs from that of free ligand P by less than 1 ppm for $P = PPh_3$, $P(p\text{-}C_6H_4Me)_3$, and PPh_2Et. These measurements were made at −70 °C to eliminate quadrupolar broadening (by copper) which interferes at higher temperatures. Under these conditions, cluster-bound and added free ligand resonances as close together as 0.2 ppm have been resolved. (b) Cryoscopic measurements have been made of phosphine titrations of "CuH" in pyridine solvent. See: Dilts, J. A.; Shriver, D. F. *J. Am. Chem. Soc.* **1969**, *91*, 4088. While these have been interpreted in terms of the unusual stoichiometry $R_3P(CuH)_2$, it appears that a higher oligomer (including a hexamer) could also be employed to fit the data.

(15) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461.

(16) Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136.

(17) Methyl formate was identified most conclusively by the small interproton coupling (J = 0.8 Hz) on both the formate (7.57 δ) and methyl (3.20 δ) protons (in C_6D_6).

(18) $P(aryl)_3$ was added to this reaction such that the overall mole ratio $P(aryl)_3/Cu$ is equal to 2.

(19) Tsuda, T.; Habu, H.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1974**, 620.

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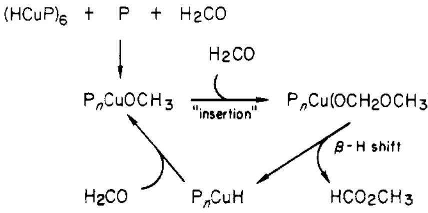
$$(1/6)(HCuP)_6 + H_2CO \rightarrow (1/n)(PCuOCH_3)_n \qquad (3)$$

troscopy) that all of the deuterium in the methyl formate product in reaction 4 is found in the methyl group. We propose the

$$H_2CO \xrightarrow{(DCuP)_6} \underset{\text{(stoichiometric)}}{HCO_2CH_2D} + \underset{\text{(catalytic)}}{HCO_2CH_3} \qquad (4)$$

following mechanism which accounts for this labeling result and employs an isoelectronic substitution (O for CH_2) in standard organometallic reaction types.



Consistent with cycles of this type, and consistent with the intermediacy of an alkoxide in the cycle, it is possible to enter the cycle from a nonhydride source[18] (reaction 5). The major points

$$(t\text{-}BuOCuPPh_3)_4{}^{20} + (H_2CO)_x \rightarrow \underset{\text{(stoichiometric)}}{HCO_2\text{-}t\text{-}Bu} + \underset{\text{(catalytic)}}{HCO_2Me} \qquad (5)$$

to be drawn from this set of observations are that a well-defined soluble copper hydride does rapidly add to an aldehydic C=O bond and that it appears to do so to form a Cu–O, rather than a Cu–C bond. As a consequence of this latter selectivity, chain growth by CO insertion into metal–carbon bonds is precluded; this accounts for the selectivity for C_1 product exhibited by the Cu/Zn/oxide catalyst.[21]

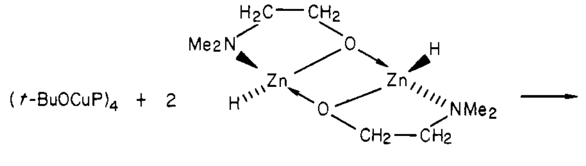
Treatment of a THF solution of $(CuO\text{-}t\text{-}Bu)_4$ containing 2 mol of P per copper with H_2 (1 atm, 25 °C) gives 60% isolated yield of $(HCuP)_6$ after 4 h; the reaction also occurs in a nonpolar solvent (benzene) and shows somewhat higher yields (80%) using 1500 psi of H_2. Vacuum transfer of the volatiles from this reaction allows detection of both resonances of Me_3COH, verified by subsequent addition of an authentic sample of this alcohol. This reaction (reaction 6), the first "hydrogenolysis" of the metal-

$$(1/4)(CuO\text{-}t\text{-}Bu)_4 + P + H_2 \rightarrow (1/6)(HCuP)_6 + t\text{-}BuOH \qquad (6)$$

alkoxide bond in a soluble complex,[24] is the analogue of the final step in a methanol synthesis, and it is the step which has been lacking in previous work with the early transition metals. The production of a metal hydride from a metal alkoxide is a new synthetic procedure and indeed confirms a proposed[25] unique characteristic of copper: formal heterolytic splitting of hydrogen (reaction 7).[26]

$$Cu^+ + H_2 \rightarrow CuH + H^+ \qquad (7)$$

In view of the proposal[9,10] that the commerical methanol catalyst involves reaction of a copper carbonyl with a zinc hydride, we have carried out a simple test of the relative stability of copper and zinc hydrides. The equimolar reaction of ZnH_2 with $HO(CH_2)_2NMe_2$ gives a complex of empirical formula $HZnO(CH_2)_2NMe_2$,[27] which we take to be a dimer by analogy to $[HZnNMe(CH_2)_2NMe_2]_2$.[28] Reaction in benzene according to reaction 8 gives rapid and complete hydride transfer from zinc to copper.



(8)

We are continuing to devise further bimetallic reactions which even more faithfully mimic the environment of heterogeneous Cu/Zn/oxide catalysts. However, the solution result in reaction 8, coupled with the high mobility of ligated hydrogen in metal cluster compounds, suggests that the site of H–H bond *scission* may differ substantially from the site of hydrogen *transfer* to bound CO, both in physical location and in the identity of the metal atom which supplies the hydride.

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(20) Tsuda, T.; Habu, H.; Horiguchi, S.; Saegusa, T. *J. Am. Chem. Soc.* **1974**, *96*, 5930.

(21) Methyl formate is produced in homogeneously catalyzed CO hydrogenation reactions employing both $HCo(CO)_4$[16,22] and $Ru(CO)_5$.[23] The intermediacy of methoxide ligands and the operation of a Tishchenko reaction merits consideration in these cases.

(22) Rathke, J. W.; Feder, H. *J. Am. Chem. Soc.* **1978**, *100*, 3623.

(23) Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419.

(24) Heterolysis of H_2 by metal acetates has been reported: White C.; Oliver, J. P.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1901.

(25) For Cu(II), see: Halpern, J.; Peters, E. *J. Chem. Phys.* **1955**, *23*, 605. For Cu(I), see: Hahn, E. A.; Peters, E. *J. Phys. Chem.* **1965**, *69*, 547. For a review, see: James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973; Chapter II.

(26) For a review of heterolytic activation of H_2, see: Brothers, P. J. *Prog. Inorg. Chem.* **1981**, *28*, 1. This review points out the difficulty of discriminating between heterolytic stoichiometry and a heterolytic mechanism; in the latter, the emerging H^+ never coordinates to the metal.

(27) This compound is nonrigid at an intermediate rate at 30 °C and thus shows broad ^1H NMR resonances. At 55 °C, the spectrum sharpens to reveal a hydride resonance at δ 4.20 (s, 1 H), methylene resonances at δ 4.00 (t, 2 H) and 2.50 (t, 2 H), and a methyl resonance at δ 2.23 (s, 6 H).

(28) Bell, N. A.; Moseley, P. T.; Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2950.

Severe Steric Hindrance: Hydrogen Bonding and the Consequences of Its Inhibition. Equilibrium Hydrogen Isotope Effects

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The effect upon proton transfer equilibria of severe steric hindrance was first observed by Brown and Kanner, who synthesized 2,6-di-*tert*-butylpyridine (**1b**) and determined that, unlike other alkylated pyridines which were more basic than pyridine (**1a**) itself, **1b** was 0.80 p*K* units less basic than the latter (in 50 vol % aqueous ethanol).[1] Gas-phase basicity measurements[2] later showed that **1b** was intrinsically *more* basic than **1a** by more than 10 kcal/mol,[3] proving that solvation effects (inhibited H bonding[4]) were responsible for the observed anomaly. The remarkable observation[2a] that **1b·H**$^+$ shows solution behavior like that of resonance-stabilized carbocations and unlike that of ammonium ions was soon followed by studies dealing with the solution and gas-phase thermodynamics of **1b** and **1b·H**$^+$ and other pyridines and pyridinium ions.[5]

The availability of *cis*-2,6-di-*tert*-butylpiperidine[6] (**2b**) and the even more severely hindered *cis*-2,6-di-*tert*-butyl-*N*-methylpiperidine[7] (**3b**) made it of interest to determine the equilibrium

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(1) Brown, H. C.; Kanner, B. *J. Am. Chem. Soc.* **1953**, *75*, 3895. *Ibid.* **1966**, *88*, 986.

(2) (a) Wolf, J. F.; Harch, P. G.; Taft, R. W. *J. Am. Chem. Soc.* **1975**, *97*, 2904. (b) Aue, D. H.; Webb, H. M.; Bowers, M. T.; Liotta, C. L.; Alexander, C. J.; Hopkins, H. P. *Ibid.* **1976**, *98*, 854.

(3) At 25 °C 1.00 p*K* unit corresponds to 1.36 kcal/mol.

(4) Arnett, E. M.; Chawla, B. *J. Am. Chem. Soc.* **1978**, *100*, 214, 217.

(5) (a) le Nobel, W.; Asano, T. *J. Org. Chem.* **1975**, *40*, 1179. (b) Hopkins, H. P.; Ali, S. Z. *J. Am. Chem. Soc.* **1977**, *99*, 2069. (c) Arnett, E. M.; Chawla, B. *Ibid.* **1979**, *101*, 7141.

(6) Day, J. C. *J. Org. Chem.* **1978**, *43*, 3646.

(7) Base **3b** is produced by reaction of **2b** with $CH_3OSO_2CF_3$. Details and characterization will be reported elsewhere.

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