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# Preparation and Characterization of Copper(I) Complexes with Unsaturated Small Molecules. Crystal Structure Determination of a Copper Carbonyl Complex Stabilized by a Tris-Chelating Oxygen Ligand

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The preparation of a series of copper carbonyl complexes [LCu(CO)] and copper olefin complexes [LCu(ethylene)] and [LCu(maleic anhydride)] from the sodium salts of the ligands $L^-$ and copper(I) compounds such as CuCl or $[Cu(CH_3CN)_4]PF_6$ is described. The copper carbonyl complexes [LCu(CO)] have also been prepared by a comproportionation reaction of copper(II) compounds $CuL_2$ with copper metal under an atmosphere of carbon monoxide. The ligands $L^-$ are anionic complexes of the type $[(C_5H_5)Co\{P(O)RR'\}_3]^-$ (R, R′ = Me, Et, Pr, Bu, Ph, OMe, OEt, OPr, OBu), $[(C_5Me_5)Co\{P(O)R_2\}_3]^-$ (R = OMe, OEt), and $[(C_5Me_5)Rh\{P(O)(OMe)_2\}_3]^-$ which act as tripodal oxygen ligands in these compounds. $[(C_5H_5)Co\{P(O)(OMe)_2\}_3Cu(CO)]$ crystallizes in space group $P2_1/c$ ($Z = 4$) with $a = 10.899$ (5) Å, $b = 12.119$ (5) Å, $c = 16.181$ (8) Å, and $\beta = 104.00$ (5)°, and its X-ray crystal structure was refined to $R_w = 0.052$ for 3788 reflections ($I > 3\sigma(I)$).

## 1. Introduction

The chemistry of copper(I) with small unsaturated molecules like carbon monoxide or olefins has interested chemists for over 100 years for a variety of reasons. An early use of copper(I) compounds is the absorption of carbon monoxide and ethylene from gas mixtures. It is remarkable that, in spite of the long use of copper(I) chloride, the composition of the active species is still subject of discussions. Some of the proposed complexes are $[CuCl(CO)(H_2O)_2]$,[1] [CuCl(CO)],[2] and $[CuCl_2(CO)]^-$.[3] The role of copper in the oxidation state +I is also discussed in the catalytic methanol syntheses from water gas.[4] Some copper(I) coordination compounds are important in bioinorganic chemistry as models for hemocyanins, which act as oxygen carriers in the blood of mollusks and arthropods.[5] Copper(I) is also supposed to be the active site in the receptors of the plant hormone ethylene.[6]

**Table I. CO Stretching Frequencies of LCuCO Complexes**

| compd | $\nu$(CO)/cm$^{-1}$ | | |
|---|---|---|---|
| $\mathrm{L_{OMe}CuCO}$ | 2075[a] | 2078[b] | 2073[c] |
| $\mathrm{L_{OEt}CuCO}$ | 2072 | 2075 | 2069 |
| $\mathrm{L_{O\text{-}\mathit{i}\text{-}Pr}CuCO}$ | 2071 | 2072 | 2067 |
| $\mathrm{L_{OBu}CuCO}$ | 2073 | 2074 | |
| $\mathrm{L_{Et}CuCO}$ | 2064 | 2062 | 2040 |
| $\mathrm{L_{Pr}CuCO}$ | 2063 | 2061 | 2051 |
| $\mathrm{L_{Bu}CuCO}$ | 2063 | 2060 | 2052 |
| $\mathrm{L_{OMe,Me}CuCO}$[d] | 2072 | 2073 | |
| $\mathrm{L_{OMe,Et}CuCO}$[d] | 2071 | 2072 | 2061 |
| $\mathrm{L_{OMe,Ph}CuCO}$[d] | 2074 | 2076 | |
| $\mathrm{L_{O\text{-}\mathit{i}\text{-}Bu,Me}CuCO}$[d] | 2070 | 2074 | |
| $\mathrm{L^*_{OMe}CuCO}$ | 2070 | 2070 | |
| $\mathrm{L^*_{OEt}CuCO}$ | 2068 | 2066 | 2059 |
| $\mathrm{L^*_{Rh,OMe}CuCO}$ | 2072 | 2072 | |

[a] Measured in hexane. [b] Dichloromethane. [c] The synthesis of ligands $L_{RR'}^-$ which have two different substituents on the phosphorus atoms produces in most cases a mixture of two diastereoisomers (see Figure 2). Their copper carbonyl complexes have identical CO stretching frequencies.

Copper(I) compounds are often unstable toward oxidation, disproportionation, and/or loss of the coordinated small molecules. So it was a challenge to prepare novel types of copper(I) compounds and learn what types of ligands could stabilize the copper carbonyl and copper olefin fragments. It is a conspicuous fact that nearly all copper(I) complexes of carbon monoxide[7] and olefins[8] are stabilized by ligands with hard donor centers from the first row of the periodic system. Among the compounds with remarkable stability are $[\{HB(pz)_3\}Cu(CO)]$[9] and [{Cu(O-*t*-Bu)(CO)}$_4$].[10] We have prepared copper(I) carbonyl and olefin complexes with tris-chelating oxygen ligands $L^-$ (Figure 1), which have ligand field properties similar to

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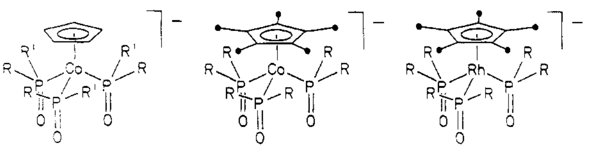

**Figure 1.** Schematic structures of the anionic complexes $[(C_5H_5)Co\{P(O)RR'\}_3]^-$ ($L_{R,R'}^-$), $[(C_5Me_5)Co\{P(O)R_2\}_3]^-$ ($L^*_R{}^-$), and $[(C_5Me_5)Rh\{P(O)R_2\}_3]^-$ ($L^*_{Rh,R}{}^-$) which act as oxygen tripod ligands and their abbreviations used in the text.

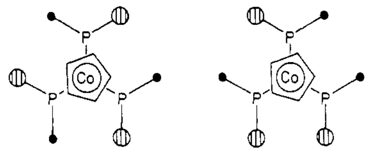

**Figure 2.** Newman projections along the cobalt–copper axis of the diastereoisomeric ligands $L_{R,R'}^-$.

the ones of fluoride and water ligands.[11]

## 2. Results and Discussion

**2.1. Oxygen Tripod Copper Carbonyl Complexes.** We have synthesized a series of LCuCO complexes as shown in Table I. Variations within the tripod ligand, e.g. variation of the ring (cyclopentadienyl or pentamethylcyclopentadienyl), of the central atom of the tripod ligand (cobalt or rhodium), and of the substituents on the phosphorus atoms (alkyl, aryl, or alkoxy groups), has only a small influence on the position of the copper carbonyl stretching frequency. Exchanging the cyclopentadienyl ring for the pentamethylcyclopentadienyl ring causes a slightly lower CO stretching frequency, and the same is true for the variation alkyl vs alkoxy substituents on the phosphorus atoms. We presume that these variations of the tripod ligands influence mainly the basicity and not the "bite" of the ligands. Steric effects of the substituents on the phosphorus atoms seem not to be important for the ground-state properties of the copper carbonyl complexes. It is interesting to note, however, that they play an important role in complexes of type $ML_2$ where the presence of two ligands L coordinated to the same metal leads to significant interligand repulsion.[12]

**Syntheses of the LCuCO Complexes.** Copper(I) halides are an often used starting material for the preparation of copper carbonyl complexes.[13] We have observed slow formation of $L_{OEt}CuCO$ upon addition of the sodium salt of the tripod ligand to a suspension of copper(I) chloride in methanol saturated with carbon monoxide gas. The yield of $L_{OEt}CuCO$ prepared by this route was ca. 50%. Alternatively, we have reacted the oxygen tripod ligands with $[Cu(ClO_4)(CO)(H_2O)_2]$[8k] in methanol, methanol/water, or methanol/pentane or with $[Cu(CH_3CN)_4]PF_6$.[14] $[Cu(CH_3CN)_4]PF_6$ forms a carbonyl complex (presumably $[Cu(CH_3CN)_3CO]^+$, $\nu(CO) = 2123$ cm$^{-1}$) in dichloromethane saturated with 1 atm of carbon monoxide but not in acetonitrile. We noticed the formation of solvent complexes also when we dissolved $[Cu(CH_3CN)_4]PF_6$ under CO in methanol ($\nu(CO) = 2108$ cm$^{-1}$) or in tetrahydrofuran ($\nu(CO) = 2095$ cm$^{-1}$). The reaction of such solutions with the sodium salts of the oxygen tripod ligands gave yields of LCuCO in the range of 80–90% when the disappearance of the carbonyl stretching band of the starting compounds was monitored carefully. Monitoring of the reaction proved necessary since the presence of small amounts of labile copper(I) solvent complexes seems to induce decomposition of the LCuCO complexes. One of the decomposition pathways is the disproportionation of copper(I). In a control experiment we discovered that $L_{OMe}CuCO$ could be prepared by comproportionation of $Cu(L_{OMe})_2$ with copper metal in methanol under an atmosphere of carbon monoxide (1 atm) (eq 1). The comproportionation reaction (eq 1) is slow. It takes several days at room temperature to bring the equilibrium completely to the right.

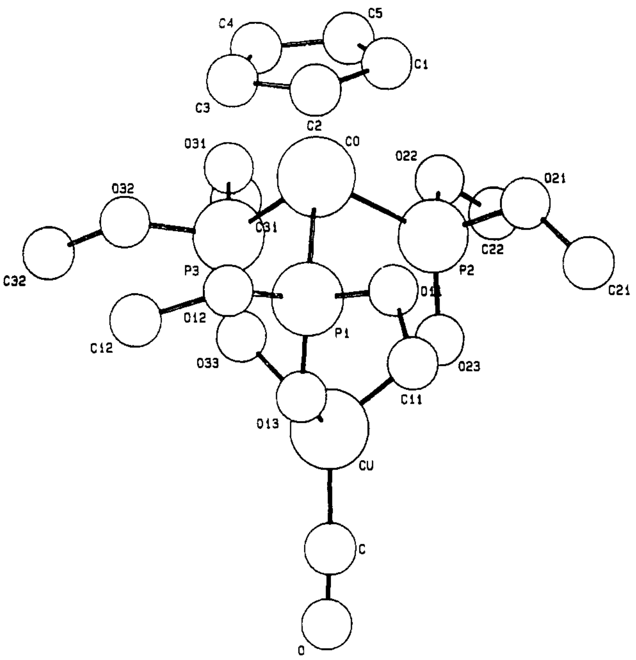

**Figure 3.** Molecular structure of $L_{OMe}CuCO$.

$$Cu(L_{OMe})_2 + Cu + 2\,CO \rightleftharpoons 2\,L_{OMe}CuCO \qquad (1)$$

**Properties of $L_{OMe}CuCO$.** This copper carbonyl complex could be prepared most conveniently from $[Cu(CH_3CN)_4]PF_6$ and $NaL_{OMe}$ or by comproportionation from copper and $Cu(L_{OMe})_2$ under an atmosphere of carbon monoxide. $L_{OMe}CuCO$ forms large yellow crystals that decompose slowly above 130 °C and melt at 160 °C. In the solid state the compound is stable at room temperature under a nitrogen atmosphere and does not lose carbon monoxide in high vacuo. In moist air the compound decomposes within a few days, giving a green product of unknown composition. It shows no CO band in the IR spectrum and is mainly not $Cu(L_{OMe})_2$. In deaerated solvents pure $L_{OMe}CuCO$ can be handled conveniently for hours, and even bubbling air through the solution for a short time causes only a light green color. The IR spectrum of this solution shows no absorptions other than those of $L_{OMe}CuCO$. The green color does not disappear, however, when CO gas is bubbled again through the solution. The coordinated carbon monoxide can easily be displaced by other ligands, for instance, phosphites, phosphines, and olefins substituted with electron-withdrawing groups like maleic anhydride and tetracyanoethylene. Substitution of the carbonyl ligand with tetramethylethylene, cyclohexene, or ethylene was not observed.

**Crystal Structure of $L_{OMe}CuCO$.** The structure of $L_{OMe}CuCO$ together with the numbering scheme is displayed in Figure 3. The main distances and angles are

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**Table II. Selected Bond Angles (deg) and Bond Distances (Å) with Their Estimated Standard Deviations**

| | | | |
|---|---|---|---|
| P(1)–Co–P(2) | 90.84 (5) | O(13)–Cu–O(23) | 93.3 (1) |
| P(1)–Co–P(3) | 94.72 (5) | O(13)–Cu–O(33) | 96.1 (1) |
| P(2)–Co–P(3) | 89.71 (5) | O(23)–Cu–O(33) | 94.4 (1) |
| Co–P(1)–O(13) | 121.2 (1) | O(13)–Cu–C | 118.8 (2) |
| Co–P(2)–O(23) | 120.7 (1) | O(23)–Cu–C | 125.4 (2) |
| Co–P(3)–O(33) | 120.9 (1) | O(33)–Cu–C | 121.5 (2) |
| Cu–O(13)–P(1) | 123.5 (2) | Cu–C–O | 176.1 (5) |
| Cu–O(23)–P(2) | 123.6 (2) | | |
| Cu–O(33)–P(3) | 124.7 (2) | | |
| Cu–O(13) | 2.033 (3) | P(1)–O(13) | 1.496 (3) |
| Cu–O(23) | 2.060 (3) | P(2)–O(23) | 1.493 (3) |
| Cu–O(33) | 2.026 (3) | P(3)–O(33) | 1.505 (3) |
| Cu–C | 1.765 (4) | C–O | 1.107 (5) |
| Co–P(1) | 2.176 (1) | | |
| Co–P(2) | 2.165 (1) | | |
| Co–P(3) | 2.160 (1) | | |

presented in Table II and the positional parameters in Table III. The oxygen tripod ligand donates six electrons to the $d^{10}$ copper(I) ion and completes together with the two electrons of the carbonyl ligand the 18-electron configuration. The coordination geometry around copper can be described as trigonal pyramidal, and the idealized molecular symmetry of the complex is $C_{3v}$. The deviation from a regular tetrahedral arrangement is significant. The O–Cu–O angles are less than the tetrahedral angle of 109.5° (93.3°, 94.4°, and 96.1°); the O–Cu–C angles range from 118.8° to 125.4°. The center of the cyclopentadienyl ring, the cobalt atom, and the Cu–C–O fragment form a nearly linear arrangement, the angles being 177.8°, 176.5°, and 176.1° respectively. The Cu–C and C–O distances of 1.765 and 1.107 Å, respectively, are consistent with other known copper carbonyl complexes whose structures have previously been determined.[7a,8a,10b,13,15] The Cu–O contacts of 2.03 and 2.06 Å are comparable to those found in $[\{Cu(O\text{-}t\text{-}Bu)(CO)\}_4]$[10b] and the polymeric compound $[Cu(C_2H_5SO_3)(CO)]$,[15a] which are, to our knowledge, the two other known structures of a copper carbonyl unit stabilized solely by oxygen ligands. The bite of the tripod ligand (nonbonding distances between the P=O oxygen atoms) ranges from 2.98 to 3.02 Å which may be compared with 3.00–3.28 Å in $NaL_{OEt}$.[16] The bond lengths and angles within the tripod ligand are in the expected range.[16]

**2.2. Oxygen Tripod Copper Olefin Complexes.** The ethylene complexes $LCu(C_2H_4)$ were prepared from the sodium salts NaL and $[Cu(CH_3CN)_4]PF_6$ under an atmosphere of ethylene in a similar manner as the carbonyl complexes. However they are significantly less stable than the carbonyl complexes and especially so when impure. Disproportionation to give metallic copper and $CuL_2$ is a main decomposition pathway in solution and in the solid state when the compounds are not perfectly dry. They decomposed slowly even under an atmosphere of ethylene when stored at −20 °C in Schlenk vessels for longer periods of time. The oxygen tripod copper(I) complexes with maleic anhydride as olefin are much easier to handle. The complexes of the type LCu(MA) (MA = maleic anhydride) were prepared by ligand exchange from the corresponding carbon monoxide or ethylene copper complexes and are stable in solution under dry nitrogen and in the solid state in dry air but decompose slowly in the presence of moisture.

**Table III. Final Positional Parameters[a] with Their Estimated Standard Deviations for $L_{OMe}CuCO$**

| atom | x | y | z | B, Å$^2$ |
|---|---|---|---|---|
| Cu | 0.73795 (6) | 0.27591 (6) | −0.30364 (4) | 3.70 (1) |
| Co | 0.77891 (6) | 0.00378 (6) | −0.18640 (4) | 3.01 (1) |
| C(1) | 0.8720 (6) | −0.1475 (5) | −0.1671 (4) | 4.4 (1) |
| C(2) | 0.7457 (6) | −0.1655 (5) | −0.1979 (4) | 5.0 (1) |
| C(3) | 0.6845 (6) | −0.1189 (6) | −0.1401 (5) | 6.7 (2) |
| C(4) | 0.7784 (8) | −0.0736 (5) | −0.0737 (4) | 7.1 (2) |
| C(5) | 0.8916 (7) | −0.0919 (5) | −0.0924 (4) | 5.6 (2) |
| P(1) | 0.6617 (1) | 0.0273 (1) | −0.3146 (1) | 3.92 (3) |
| O(11) | 0.7217 (4) | −0.0518 (4) | −0.3742 (3) | 5.4 (1) |
| C(11) | 0.6742 (6) | −0.0506 (6) | −0.4629 (4) | 5.7 (2) |
| O(12) | 0.5283 (4) | −0.0333 (4) | −0.3287 (3) | 5.8 (1) |
| C(12) | 0.4223 (6) | 0.0233 (7) | −0.3106 (4) | 5.9 (2) |
| O(13) | 0.6366 (4) | 0.1401 (3) | −0.3525 (3) | 4.70 (9) |
| P(2) | 0.9327 (1) | 0.0934 (1) | −0.2186 (1) | 4.06 (3) |
| O(21) | 1.0243 (4) | 0.0142 (5) | −0.2522 (3) | 9.4 (1) |
| C(21) | 1.0476 (7) | 0.0180 (7) | −0.3311 (4) | 7.2 (2) |
| O(22) | 1.0248 (4) | 0.1289 (4) | −0.1284 (3) | 6.7 (1) |
| C(22) | 1.1163 (7) | 0.2085 (6) | −0.1233 (5) | 6.4 (2) |
| O(23) | 0.9072 (3) | 0.1918 (3) | −0.2758 (2) | 4.11 (8) |
| P(3) | 0.7176 (1) | 0.1538 (1) | −0.13655 (8) | 3.58 (3) |
| O(31) | 0.8011 (5) | 0.1740 (4) | −0.0420 (3) | 5.6 (1) |
| C(31) | 0.8515 (7) | 0.2768 (6) | −0.0109 (4) | 5.7 (2) |
| O(32) | 0.5820 (4) | 0.1255 (4) | −0.1183 (3) | 5.05 (9) |
| C(32) | 0.5153 (6) | 0.2076 (6) | −0.0847 (4) | 5.7 (2) |
| O(33) | 0.7107 (4) | 0.2608 (3) | −0.1847 (2) | 4.61 (9) |
| C | 0.7088 (5) | 0.4013 (5) | −0.3604 (3) | 4.0 (1) |
| O | 0.6837 (5) | 0.4782 (4) | −0.3976 (3) | 6.6 (1) |

| atom | x | y | z |
|---|---|---|---|
| H(1) | 0.936 | −0.170 | −0.194 |
| H(2) | 0.706 | −0.202 | −0.249 |
| H(3) | 0.596 | −0.119 | −0.144 |
| H(4) | 0.765 | −0.037 | −0.025 |
| H(5) | 0.971 | −0.069 | −0.059 |
| H(111) | 0.721 | −0.101 | −0.488 |
| H(112) | 0.588 | −0.071 | −0.476 |
| H(113) | 0.682 | 0.022 | −0.484 |
| H(121) | 0.351 | −0.025 | −0.324 |
| H(122) | 0.441 | 0.041 | −0.252 |
| H(123) | 0.404 | 0.089 | −0.343 |
| H(211) | 1.107 | −0.037 | −0.336 |
| H(212) | 0.970 | 0.004 | −0.372 |
| H(213) | 1.079 | 0.088 | −0.342 |
| H(221) | 1.160 | 0.219 | −0.066 |
| H(222) | 1.174 | 0.185 | −0.155 |
| H(223) | 1.079 | 0.276 | −0.146 |
| H(311) | 0.897 | 0.269 | 0.047 |
| H(312) | 0.907 | 0.302 | −0.044 |
| H(313) | 0.785 | 0.329 | −0.014 |
| H(321) | 0.437 | 0.179 | −0.078 |
| H(322) | 0.565 | 0.230 | −0.031 |
| H(323) | 0.499 | 0.269 | −0.122 |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)\,[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Preliminary experiments have shown that a series of other alkene complexes are accessible from the ethylene compounds. Electron-withdrawing substituents on the carbon–carbon double bond seem, however, to be a prerequisite for these copper(I) alkene complexes to be stable. We have noticed that the ν(P=O) frequency of the oxygen tripod unit in the olefin and carbonyl complexes correlates roughly with the stability of the compounds. The following series may illustrate the range (~1130–1170 cm$^{-1}$) of ν(P=O) frequencies that we observe LCu(MA) < LCuCO < $LCu(C_2H_4)$ ≪ NaL. We have found in other types of complexes also that the ν(P=O) frequency is a sensitive probe for the charge density on the metal ion.[17] It is interesting to note that electron-withdrawing substituents

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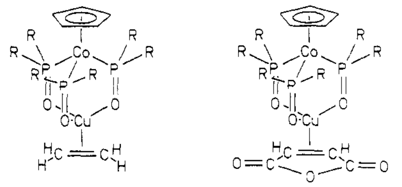

**Figure 4.** Schematic structures of the olefin complexes LCu($C_2H_4$) and LCu(MA).

on the olefin clearly stabilize the complexes of the type LCu(olefin) whereas the opposite effect has been found in general[18] in copper olefin complexes.

The $^1H$ NMR spectra of the olefin complexes LCu($C_2H_4$) and LCu(MA) are deceptively simple. The six R groups appear isochronous as if the molecules had $C_{3v}$ symmetry; e.g., the signal of the 18 $OCH_3$ protons in $L_{OMe}$Cu(MA) is a simple virtual quartet. Furthermore the ethylene protons give rise to a singlet. This is not compatible with a static structure as depicted in Figure 4. The highest possible symmetry of these molecules is $C_s$. The six R groups should therefore give rise to three different groups of signals, and the spectrum of the olefin protons of the coordinated ethylene should be of the type AA′BB′. Obviously the rotation of the ethylene ligand relative to the oxygen tripod ligand is rapid on the NMR time scale at room temperature. This is in accord with extended Hückel molecular orbital calculations which show that the alkene rotational barrier in $d^{10}$ complexes of the type [(two-electron ligand)$_3$M(alkene)] should indeed be rather low.[19]

The $^1H$ NMR spectra of the oxygen tripod complexes $L_R$Cu($C_2H_4$) under an ethylene atmosphere show that in addition to the olefin rotation an exchange between free and coordinated ethylene takes place. The exchange is rapid relative to the NMR time scale at room temperature in the complexes $L_{OMe}$Cu($C_2H_4$) and $L_{OEt}$Cu($C_2H_4$). In the complex $L_{O\text{-}i\text{-}Pr}$Cu($C_2H_4$), however, the six bulky isopropoxy groups are shielding the copper center more effectively so that the ethylene exchange at room temperature becomes slow on the NMR time scale.

## 3. Concluding Remarks

We have shown in this paper that the oxygen tripod ligands $L^-$ form surprisingly stable copper carbonyl complexes. Our qualitative study of the disproportionation/comproportionation equilibrium

$$CuL_2 + Cu + 2\,CO \rightleftharpoons 2\,LCuCO$$

indicates, however, that the formation of the copper carbonyl complexes $L_R$CuCO is only slightly favored thermodynamically. The *kinetic* stability which seems very important could be imposed by the geometry of the tripod ligands $L^-$. These ligands are not flexible enough to allow a trigonal-planar coordination of the copper ion but would force the copper ion in the initial decarbonylation product LCu (eq 2) in an energetically unfavorable trigonal-py-

$$LCuCO \rightarrow LCu + CO \qquad (2)$$

ramidal geometry. The activation enthalpy of such a decarbonylation reaction could therefore be relatively high compared to, e.g., the decarbonylation of the elusive $CuCO^+$ (aq) complex.[20]

Variation of the size of the six R substituents in the tripod ligands has no influence on the electronic properties of the ligands as judged from the copper carbonyl stretching frequencies. It does influence, however, the rate of exchange of the ethylene ligand in the $L_R$Cu($C_2H_4$) complexes. From the crystal structure of $L_{OMe}$CuCO and from models of the LCuCO compounds one can see that the copper center is much better shielded by the six $OCH(CH_3)_2$ groups in $L_{O\text{-}i\text{-}Pr}$CuCO than by the six $OCH_3$ or $OC_2H_5$ substituents in $L_{OMe}$CuCO and $L_{OEt}$CuCO. So far we have no quantitative data on the kinetics and the mechanism of the olefin exchange, but the observed influence of the size of the R substituents on the rate of exchange is in accord with an associative mechanism. Furthermore we have preliminary NMR data which indicate that the rate of olefin exchange is dependent on the concentrations of both the copper olefin complex and the free olefin.

**Table IV. Reaction Conditions and Yields for the Preparation of the CoL$_2$ Complexes**

| | mol ratio[a] | rt[b] | t[c] | y[d] |
|---|---|---|---|---|
| Co($L_{OMe,Me}$)$_2$ | 1:4 | 50 | 100 | 50 |
| Co($L_{OMe,Et}$)$_2$ | 1:3 | 40 | 120 | 80 |
| Co($L_{OMe,Ph}$)$_2$ | 1:5 | 24 | 100 | 76 |
| Co($L_{O\text{-}i\text{-}Bu,Me}$)$_2$ | 1:2.5 | 20 | 120 | 19 |

[a] Molar ratio of reactants ($CoCp_2$:phosphonous acid monoester). [b] Reaction time (h). [c] Reaction temperature (°C). [d] Yield (%).

## 4. Experimental Section

**4.1. General Details.** All reactions were performed under dry nitrogen in conventional Schlenk glassware unless otherwise quoted. Infrared spectra were recorded on a Perkin-Elmer PE 580 spectrometer. The CO stretching frequencies were measured by using the rotational lines of dilute gaseous deuterium chloride for calibration.[21] The frequencies reported in Table I are estimated to be accurate to ±1 $cm^{-1}$. $^1H$ NMR spectra were obtained on a Bruker WP80 (80 MHz) or Varian Aspect EM 360A (60 MHz) NMR spectrometer at room temperature. Chemical shifts are given in parts per million (positive downfield) relative to $Me_4Si$ (organic solvents) or $Me_3SiCD_2CD_2COONa$ (water). Electron-impact (70 eV) mass spectra were run on a Varian MAT CH5 spectrometer. C, H analyses were performed on a Carlo Erba Elementar Analizer Model 1106. Membrane filters (regenerated cellulose, 1.0 μm, Schleicher & Schuell, RC60) were used to filter off small particles. Methylphosphonous acid monoisobutyl ester was a gift from Hoechst AG, Knapsack. Dicyclopentadienylcobalt[22] was freshly sublimed prior to use. Tetrakis(acetonitrile)copper(I) hexafluorophosphate,[14] ethylphosphonous acid monomethyl ester,[23] phenylphosphonous acid monomethyl ester,[24] Co($L_{OMe}$)$_2$,[25] Cu($L^*_{Rh,OMe}$)$_2$,[11] Na$L_{OEt}$,[26] Na$L_{O\text{-}i\text{-}Pr}$, Na$L_{OBu}$,[27] Na$L_{Et}$,[28] and Na$L^*_{OEt}$[29] were prepared according to the published procedures. Na$L_{Pr}$ and Na$L_{Bu}$ were prepared according to the procedure given for Na$L_{Et}$.[28] Methylphosphonous acid monomethyl ester was prepared in the same manner as ethylphosphonous acid monomethyl ester.

**4.2. Preparation of the ML$_2$ Complexes.** The cobalt(II) complexes Co($L_{OMe,Me}$)$_2$, Co($L_{OMe,Et}$)$_2$, Co($L_{OMe,Ph}$)$_2$, and Co-

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**Table V. Reaction Conditions and Yields for the Preparation of the Sodium Salts of the Oxygen Tripod Ligands $L^-$ from the Cobalt Complexes $CoL_2$**

| | mol ratio[a] | rt[b] | y[c] |
|---|---|---|---|
| $NaL_{OMe,Me}$ | 1:7 | 25 | 68 |
| $NaL_{OMe,Et}$ | 1:7 | 50 | 84 |
| $NaL_{OMe,Ph}$ | 1:6.3 | 120 | 93 |
| $NaL_{O\text{-}i\text{-}Bu,Me}$ | 1:7 | 40 | 90 |

[a] Molar ratio of reactants ($CoL_2$:NaCN). [b] Reaction time (h). [c] Yield (%).

$(L_{O\text{-}i\text{-}Bu,Me})_2$ were synthesized according to the procedure described for the preparation of $Co(L_{O\text{-}i\text{-}Pr})_2$.[27] Reaction time, temperature and yields are given in Table IV. $Co(L_{OMe,Me})_2$, $Co(L_{OMe,Et})_2$, and $Co(L_{O\text{-}i\text{-}Bu,Me})_2$ were recrystallized from dichloromethane/acetone.

**$[Co\{(C_5H_5)Co[P(O)(OMe)(Me)]_3\}_2]$ ($Co(L_{OMe,Me})_2$):** IR (KBr, $cm^{-1}$) 1114 (vs, $\nu$(P=O)); MS, *m/e* 865 ($M^+$). Anal. Calcd for $C_{22}H_{46}Co_3O_{12}P_6$: C, 30.54; H, 5.36. Found: C, 30.68; H, 5.39.

**$[Co\{(C_5H_5)Co[P(O)(OMe)(Et)]_3\}_2]$. ($Co(L_{OMe,Et})_2$):** IR (KBr, $cm^{-1}$) 1111 (vs, $\nu$(P=O)); MS, *m/e* 949 ($M^+$). Anal. Calcd for $C_{28}H_{58}Co_3O_{12}P_6$: C, 35.42; H, 6.16. Found: C, 35.07; H, 6.16.

**$[Co\{(C_5H_5)Co[P(O)(OMe)(Ph)]_3\}_2]$ ($Co(L_{OMe,Ph})_2$):** IR (KBr, $cm^{-1}$) 1116 (vs, $\nu$(P=O)), 1093 (s, $\nu$(P=O)); MS, *m/e* 1237 ($M^+$). Anal. Calcd for $C_{52}H_{58}Co_3O_{12}P_6$: C, 50.46; H, 4.72. Found: C, 50.39; H, 4.82.

**$[Co\{(C_5H_5)Co[P(O)(O\text{-}i\text{-}Bu)(Me)]_3\}_2]$ ($Co(L_{O\text{-}i\text{-}Bu,Me})_2$):** IR (KBr, $cm^{-1}$) 1113 (vs, $\nu$(P=O)).

**$[Cu\{(C_5H_5)Co[P(O)(OMe)_2]_3\}_2]$ ($Cu(L_{OMe})_2$).** $NaL_{OMe}$ (3.64 g, 7.7 mmol) and 0.94 g (3.8 mmol) of $CuSO_4{\cdot}5H_2O$ were refluxed in 150 mL of methanol in air for 1 h. The precipitated sodium sulfate was filtered from the hot solution. Storing this solution at −20 °C for 2 days yielded yellow crystals that were dried in high vacuo. The yield was 3.48 g (94%). The compound is identical with $Cu(L_{OMe})_2$ prepared by an alternative route:[11] IR (KBr, $cm^{-1}$) 1104 (vs, $\nu$(P=O)), 1142 (vs, $\nu$(P=O)), 580 (m), 610 (m, $\delta$(P=O)). Anal. Calcd for $C_{22}H_{46}Co_2CuO_{18}P_6$: C, 27.36; H, 4.80. Found: C, 27.40; H, 4.84.

**4.3. Preparation of the Sodium Salts of the Oxygen Tripod Ligands. General Procedure.** To a stirred suspension of ca. 2 g of the cobalt complex $Co(L_R)_2$ in 70 mL of methanol was added a slight excess of NaCN. The reaction mixture was stirred in air for several hours at room temperature until a sample of the mixture was completely soluble in water. The solution was taken to dryness and extracted with dry dichloromethane to remove the excess of NaCN and some insoluble byproducts. The solvent was distilled off and the resulting yellow-orange powder dried in high vacuo. For further purification the products (except $NaL_{O\text{-}i\text{-}Bu,Me}$, see below) were redissolved in methanol/water and filtered, concentrated, and dried in high vacuo. Reaction conditions and yields are given in Table V.

**$Na[(C_5H_5)Co\{P(O)(OMe)(Me)\}_3]$ ($NaL_{OMe,Me}$):** IR (KBr, $cm^{-1}$) 1142 (vs, $\nu$(P=O)); MS, *m/e* 426 ($M^+$); $^1H$ NMR (60 MHz, $CDCl_3$) $\delta$ 4.78, 4.80 (2s, 5, $C_5H_5$), 3.5 (virt m, 9, $OCH_3$), 1.7 (virt m, 9, $CH_3$), 4.1 (s, br, $H_2O$). Anal. Calcd for $C_{11}H_{25}CoNaO_7P_3$: C, 29.75; H, 5.67. Found: C, 30.07; H, 5.66.

**$Na[(C_5H_5)Co\{P(O)(OMe)(Et)\}_3]$ ($NaL_{OMe,Et}$):** IR (KBr, $cm^{-1}$) 1136 (vs, $\nu$(P=O)); MS, *m/e* 468 ($M^+$); $^1H$ NMR (60 MHz, $CDCl_3$) $\delta$ 4.6, 4.8 (2s, 5, $C_5H_5$), 3.6 (virt m, 9, $OCH_3$), 2.0 (m, 6, $CH_2$), 1.1 (m, 9, $CH_3$), 4.0 (s, br, $H_2O$). Anal. Calcd for $C_{14}H_{31}CoNaO_7P_3$: C, 34.58; H, 6.43. Found: C, 34.17; H, 6.48.

**$Na[(C_5H_5)Co\{P(O)(OMe)(Ph)\}_3]$ ($NaL_{OMe,Ph}$):** IR (KBr, $cm^{-1}$) 1146 (s, br, $\nu$(P=O)); MS, *m/e* 612 ($M^+$); $^1H$ NMR (60 MHz, $CD_2Cl_2$) $\delta$ 4.5, 4.6 (2s, 5, $C_5H_5$), 3.2, 3.6 (2 virt m, 9, $OCH_3$), 7.1–7.7 (m, 15, $C_6H_5$), 4.0 (s, br, $H_2O$). Anal. Calcd for $C_{26}H_{31}CoNaO_7P_3$: C, 49.54; H, 4.96. Found: C, 49.47; H, 4.92.

**$Na[(C_5H_5)Co\{P(O)(O\text{-}i\text{-}Bu)(Me)\}_3]$ ($NaL_{O\text{-}i\text{-}Bu,Me}$).** The sodium salt was dissolved in ether and dichloromethane (1:1) and the solution filtered and taken to dryness. The sticky residue was taken up in water and the resulting turbid solution filtered through a membrane. Water was distilled off and the yellow powder dried in high vacuo. The product is very hygroscopic: IR (KBr, $cm^{-1}$) 1140 (vs, $\nu$(P=O)); $^1H$ NMR (80 MHz, $CDCl_3$) $\delta$ 4.9, (s, 5, $C_5H_5$), 3.4–3.9 (m, 6, $OCH_2CH(CH_3)_2$), 1.7 (virt m, 9, $PCH_3$), 1.8 (m, 3, $OCH_2CH(CH_3)_2$), 0.9 (d, 18, $^3J$(HCCH) = 7 Hz, $OCH_2CH(CH_3)_2$). Anal. Calcd for $C_{20}H_{41}CoNaO_6P_3$: C, 43.49; H, 7.48. Found: C, 43.33; H, 7.89.

**$Na[(C_5Me_5)Co\{P(O)(OMe)_2\}_3]$ ($NaL^*_{OMe}$).** This compound was prepared by analogy with the procedure given for $NaL^*_{OEt}$[29] as a yellow powder. It is soluble in methanol, hexane, ether, and dichloromethane and slightly soluble in water. Purification and recrystallization using Soxhlet extraction with dichloromethane gave large yellow crystals: IR (KBr, $cm^{-1}$) 1157 (vs, $\nu$(P=O)), 576 (vs, $\delta$(P=O)); $^1H$ NMR (80 MHz, $CDCl_3$) $\delta$ 3.9 (s, br, $H_2O$), 1.6 (q, 15, $^4J$(HCCCoP) = 1.6 Hz, $C_5(CH_3)_5$), 3.5 (virt q, 18, $^3J$(POCH) = 10 Hz, $POCH_3$). Anal. Calcd for $C_{16}H_{33}CoNaO_9P_3{\cdot}{}^4/_3H_2O$: C, 33.82; H, 6.33. Found: C, 33.66; H, 6.11.

**$Na[(C_5H_5)Co\{P(O)(OMe)_2\}_3]$ ($NaL_{OMe}$).** This compound has been synthesized on a small scale[27] according to the general procedure given above for the preparation of the sodium salts of the oxygen tripod ligands. On a larger scale side reactions become predominant. We have found that cobalt(II), perhaps in the form of $[Co(CN)_5]^{3-}$, strongly catalyzes the reaction of $NaL_{OMe}$ with sodium cyanide to give mainly $Na[(C_5H_5)Co\{P(O)(OMe)_2\}(CN)_2]$.

**$Na[(C_5H_5)Co\{P(O)(OMe)_2\}(CN)_2]$:** IR (KBr, $cm^{-1}$) 2111 (s, $\nu$(C≡N)), 2118 (s, $\nu$(C≡N)), 1141 (s, $\nu$(P=O)); $^1H$ NMR (80 MHz, $D_2O$) $\delta$ 5.4 (q, 5, $^3J_{HCCoP}$ = 0.3 Hz, $C_5H_5$), 3.7 (d, $^3J_{HCOP}$ = 11 Hz, $OCH_3$). Anal. Calcd for $C_9H_{11}CoN_2NaO_3P{\cdot}H_2O$: C, 33.15; H, 4.02; N, 8.59. Found: C, 33.53; H, 3.60; N, 8.78.

For the preparation of $NaL_{OMe}$ from the reaction of $Co(L_{OMe})_2$ with NaCN it is therefore essential that air oxidation prevents the accumulation of the intermediate $[Co(CN)_5]^{3-}$. A suspension of 23.6 g (24.6 mmol) of $Co(L_{OMe})_2$ in 200 mL of methanol was cooled with an ice bath. While air was bubbled through the mixture, a total of 8.4 g (171.4 mmol) of NaCN was added in small portions over a period of 1 h. A clear solution was formed, and the color turned from yellow to deep orange. The solvent was removed with a rotary evaporator and the resulting orange residue dried in high vacuo. Extraction of the powder with dichloromethane in a Soxhlet apparatus was used to remove $Na_3[Co(CN)_6]$ and excess NaCN. The product $NaL_{OMe}$ obtained as a bright yellow powder after distilling off the dichloromethane and drying in high vacuo (yield 22.5 g, 97%) is pure enough for most purposes. If necessary, $NaL_{OMe}$ can be dissolved in twice-distilled water and the solution filtered through a membrane. Orange crystals could be grown by suspending the yellow powder in refluxing acetone and adding small portions of methanol until all of the solid had dissolved. The solution was the cooled overnight to −20 °C: IR (KBr, $cm^{-1}$) 1170 (vs, $\nu$(P=O)), 582 (s, $\delta$(P=O)); $^1H$ NMR (80 MHz, $CD_3OD$) $\delta$ 5.1 (q, 5, $^3J_{HCCoP}$ = 0.5 Hz, $C_5H_5$), 3.6 (virt q, 18, $^3J_{HCOP}$ = 11 Hz, $OCH_3$). $NaL_{OMe}$ is very soluble in water, methanol, and dichloromethane and only slightly soluble in hexane, acetone, and ether.

**4.4. Preparation of the Copper(I) Carbonyl and Olefin Complexes. $[(C_5H_5)Co\{P(O)(OMe)_2\}_3Cu(CO)]$ ($L_{OMe}CuCO$). Method 1.** $[Cu(CH_3CN)_4]PF_6$ (1.44 g, 3.9 mmol) was dissolved in 40 mL of dichloromethane, saturated with carbon monoxide, and stirred for 30 min. An IR spectrum of the solution showed a $\nu$(CO) vibration at 2123 $cm^{-1}$. After addition of 1.83 g (3.9 mmol) of $NaL_{OMe}$ which caused the precipitation of $NaPF_6$, the IR spectrum of the solution showed only one CO absorption at 2078 $cm^{-1}$. The precipitate was filtered off, and the dichloromethane solution was evaporated to leaves a yellow powder. The product was dried in high vacuo, dissolved in 20 mL of ether saturated with carbon monoxide at room temperature, and filtered through a membrane. After 2 days at −20 °C yellow crystals had grown from the ether solution. The crystallization was completed at −78 °C. The light yellow solution was decanted, and the crystals were washed with small portions of cold ether and dried in high vacuo. Yield: 1.93 g of $L_{OMe}CuCO$ (92%).

**Method 2.** $Cu(L_{OMe})_2$ (2.44 g, 2.5 mmol) and 0.5 g (7.9 mmol) of copper powder were suspended in 60 mL of methanol, saturated with carbon monoxide, and stirred until the CO band at 2086 $cm^{-1}$ did not increase any more (ca. 2 days). The solution was filtered from the excess of copper and the methanol distilled off. The obtained yellow powder was redissolved in ether, saturated with carbon monoxide at room temperature, and filtered again. Working up as described above yielded 1.85 g of $L_{OMe}CuCO$ (67%): IR (KBr, $cm^{-1}$) 2073 (vs, $\nu$(CO)), 1138 (vs, $\nu$(P=O)), 585 (s, $\delta$-(P=O)). $^1H$ NMR (80 MHz, $CDCl_3$) $\delta$ 5.0 (q, 5, $^3J_{HCCoP}$ = 0.2 Hz, $C_5H_5$), 3.7 (virt q, 18, $^3J_{HCOP}$ = 11 Hz, $OCH_3$). Anal. Calcd for $C_{12}H_{23}CoCuO_{10}P_3$: C, 26.56; H, 4.27. Found: C, 26.56; H, 4.36.

**Table VI. Crystal Data for $L_{OMe}$CuCO**

| | |
|---|---|
| empirical formula | $C_{12}H_{23}CoCuO_{10}P_3$ |
| molar mass | 542.71 |
| cryst symmetry | monoclinic |
| space group | $p2_1/c$, No. 14 |
| cell dimens (esds) | |
| *a*, Å | 10.899 (5) |
| *b*, Å | 12.119 (5) |
| *c*, Å | 16.181 (8) |
| *β*, deg | 104.00 (5) |
| V, Å$^3$ | 2074 (3) |
| *Z* (molecules/cell) | 4 |
| *d* (calcd), g/cm$^3$ | 1.73 |
| abs coeff, cm$^{-1}$ | $\mu$(Mo K$\alpha$) = 20.98 |
| cryst shape | irreg fragment, largest diameter 0.5 mm |
| wavelength (Mo/K$\alpha$), Å | 0.710 69 |
| monochromator | graphite |
| scan range, deg | $0.1 < \theta < 30$ |
| temp | room temp |
| no. of reflctns collected | 6596 |
| no. of unique intensities | 4462 ($I > n\sigma(I)$ ($n$ = 1)) |
| no. of reflctns ($I > 3\sigma(I)$) | 3788 |
| no. of parameters | 244 |
| *R* | 5.2 |
| $R_w$, weighting scheme ($w$ = 1) | 5.2 |
| esd | 1.86 |
| residual electron density, e Å$^{-3}$ | 0.9 |

$L_{OMe}$CuCO is very soluble in methanol, dichloromethane, and toluene, soluble in acetone and ether, and only slightly soluble in water and hexane at room temperature.

**[(C$_5$Me$_5$)Rh{P(O)(OMe)$_2$}$_3$Cu(CO)] (L*$_{Rh,OMe}$CuCO)** was prepared by comproportionation of Cu(L*$_{Rh,OMe}$)$_2$[11] and copper in methanol saturated with carbon monoxide. It was worked up as described for $L_{OMe}$CuCO (see above).

The other copper carbonyl complexes listed in Table I were prepared from [Cu(CH$_3$CN)$_4$]PF$_6$ and the sodium salt of the corresponding oxygen tripod ligand in dichloromethane as described for $L_{OMe}$CuCO. All copper carbonyl complexes have the same color as the sodium salts of the parent ligands; i.e., they are yellow except for L*$_{Rh,OMe}$CuCO which is colorless.

**[(C$_5$H$_5$)Co{P(O)(O-*i*-Pr)$_2$}$_3$Cu(C$_2$H$_4$)] ($L_{O\text{-}i\text{-}Pr}$Cu(C$_2$H$_4$)).** Na$L_{O\text{-}i\text{-}Pr}$ (321.2 mg, 0.5 mmol) was added to a well-stirred mixture of 10 mL of pentane and 10 mL of water under an atmosphere of ethylene. The sodium salt dissolved in the pentane phase. After 186.4 mg (0.5 mmol) of [Cu(CH$_3$CN)$_4$]PF$_6$ was added, the solution was stirred for 30 min and the water phase then removed. The organic phase was washed twice with 5 mL of water and dried with molecular sieve (4 Å) under an ethylene atmosphere. Pentane was distilled off at −78 °C in high vacuo and the resulting yellow powder dried for another 3 h, yielding 277.8 mg of $L_{O\text{-}i\text{-}Pr}$Cu(C$_2$H$_4$) (78%). The product when exposed to air turns rapidly green. A sample stored at −20 °C in a Schlenk vessel under ethylene decomposed after a few days. When the product is contaminated with traces of solvent, it disproportionates to Cu($L_{O\text{-}i\text{-}Pr}$)$_2$ and metallic copper. In solution under nitrogen atmosphere it can be handled only for a short period (~1 h): IR (pentane, cm$^{-1}$) 1155 ($\nu$(P=O); $^1$H NMR (80 MHz, benzene-$d_6$) $\delta$ 5.1 (m, 6, OC*H*(CH$_3$)$_2$), 5.0 (q, 5, $^3J_{HCCoP}$ = 0.4 Hz, C$_5$H$_5$), 4.0 (s, 4, C$_2$H$_4$), 1.4, 1.3 (2d, 36, $^3J_{HCCH}$ = 6 Hz, OCH(C*H*$_3$)$_2$). Anal. Calcd for $C_{25}H_{51}CoCuO_9P_3$: C, 42.23; H, 7.23. Found: C, 41.48; H, 7.16.

**[(C$_5$H$_5$)Co{P(O)(OEt)$_2$}$_3$Cu(C$_2$H$_4$)] ($L_{OEt}$Cu(C$_2$H$_4$)).** From 250 mg (0.45 mmol) of Na$L_{OEt}$ and 158.9 mg (0.43 mmol) of [Cu(CH$_3$CN)$_4$]PF$_6$ as described for $L_{O\text{-}i\text{-}Pr}$Cu(C$_2$H$_4$). Yield: 205 mg (76%) of a yellow powder. The $L_{OEt}$Cu(C$_2$H$_4$) complex prepared in this way is more labile than $L_{O\text{-}i\text{-}Pr}$Cu(C$_2$H$_4$); we could not get a correct elemental analysis; IR (pentane, cm$^{-1}$) 1144 ($\nu$(P=O)); $^1$H NMR (80 MHz, benzene-d$_6$) $\delta$ 5.1 (s, 5, C$_5$H$_5$), 4.3 (virt m, 12, POC*H*$_2$CH$_3$), 4.1 (s, 4, C$_2$H$_4$), 1.3 (t, 18, $^3J_{HCCH}$ = 7 Hz, POCH$_2$C*H*$_3$).

**[(C$_5$H$_5$)Co{P(O)(O-*i*-Pr)$_2$}Cu(MA)] ($L_{O\text{-}i\text{-}Pr}$Cu(MA)).** Maleic anhydride (7.6 mg, 0.08 mmol) was added to a solution of 54.8 mg (0.08 mmol) of $L_{O\text{-}i\text{-}Pr}$Cu(C$_2$H$_4$) in 5 mL of pentane. The color of the solution changed rapidly from yellow to orange. After 1 h the solution was filtered through a membrane and the pentane slowly removed with a light stream of nitrogen gas. The bright orange crystals thus obtained were dried in high vacuo. The yield of $L_{O\text{-}i\text{-}Pr}$Cu(MA) was 54.8 mg (91%): IR (KBr, cm$^{-1}$) 1838 (m, $\nu_{sy}$(CO)), 1773 (s, $\nu_{asy}$(CO)), 1145 (s, $\nu$(P=O)), 578 (s, $\delta$(P=O)); $^1$H NMR (80 MHz, benzene) $\delta$ 5.0 (m, 6, OC*H*(CH$_3$)$_2$), 4.9 (q, 5, $^3J_{HCCoP}$ = 0.4 Hz, C$_5$H$_5$), 4.6 (s, 2, C$_4$H$_2$O$_3$), 1.30, 1.33 (2d, 36, $^3J_{HCCH}$ = 6 Hz, OCH(C*H*$_3$)$_2$). Anal. Calcd for $C_{27}H_{49}CoCuO_{12}P_3$: C, 41.52; H, 6.32. Found: C, 41.51; H, 6.52.

**[(C$_5$H$_5$)Co{P(O)(OMe)$_2$}$_3$Cu(MA)] ($L_{OMe}$Cu(MA)).** Maleic anhydride (0.10 g, 1.02 mmol) and 0.50 g (1.05 mmol) of Na$L_{OMe}$ were added to a solution of 0.37 g (1.00 mmol) of [Cu(CH$_3$CN)$_4$]PF$_6$ in 20 mL of dichloromethane. The orange-red solution was filtered from NaPF$_6$ with a membrane and taken to dryness. The resulting orange powder was washed with small portions of methanol and pentane. Orange crystals could be obtained by diffusion of hexane in a saturated solution of $L_{OMe}$Cu(MA) in dichloromethane. The yield was 0.23 g (38%) of $L_{OMe}$Cu(MA): IR (KBr, cm$^{-1}$) 1837 (m, $\nu_{sy}$(CO)), 1778 (s, $\nu_{asy}$(CO)), 1131 (s, $\nu$(P=O)), 590 (s, $\delta$(P=O)); $^1$H NMR (80 MHz, toluene-$d_8$) $\delta$ 4.8 (q, 5, $^3J_{HCCoP}$ = 0.4 Hz, C$_5$H$_5$), 4.5 (s, 2, C$_4$H$_2$O$_3$), 3.5 (virt q, 18, $^3J_{HOCP}$ = 11 Hz, OCH$_3$). Anal. Calcd for $C_{15}H_{25}CoCuO_{12}P_3$: C, 29.40; H, 4.11. Found: C, 29.29; H, 4.17.

**4.5. X-ray Diffraction Data.** A suitable crystal of $L_{OMe}$CuCO was obtained by fragmentation of a large crystal grown from diethyl ether. It was investigated by Weissenberg and precession photographs that showed the unit cell to be monoclinic, space group $P2_1/c$. Data were collected on an Enraf-Nonius CAD4-diffractometer; parameters are given in Table VI. The structure was solved by a combination of direct methods and Fourier techniques using the programs SDP,[30] MULTAN 11/82,[31,32] and DIFABS[33] for absorption correction on a VAX 11/730 computer (Digital Equipment Corp.). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions ($d_{c-H}$ = 0.95 Å) and treated as riding atoms with fixed thermal parameters ($B_{iso}$ = 5.0 Å$^2$). The structure was refined by full-matrix least-squares techniques leading to final values of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.052$ and $R_w = (\sum(|F_o| - |F_c|)^2/\sum F_o^2)^{0.5} = 0.052$ using unit weights.

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**Registry No.** MA, 108-31-6; Co($L_{OMe,Me}$)$_2$, 113793-03-6; Co($L_{OMe,ET}$)$_2$, 113779-67-2; Co($L_{OMe,Ph}$)$_2$, 113779-68-3; Co($L_{O\text{-}i\text{-}Bu,Me}$)$_2$, 113779-69-4; CoCp$_2$, 1277-43-6; Cu($L_{OMe}$)$_2$, 58438-16-7; Cu(L*$_{Rh,OMe}$)$_2$, 82867-82-1; Cu($L_{O\text{-}i\text{-}Pr}$)$_2$, 110935-64-3; $L_{OMe}$CuCO, 113779-76-3; L*$_{Rh,OMe}$CuCO, 113779-77-4; $L_{OEt}$CuCO, 113779-78-5; $L_{O\text{-}i\text{-}Pr}$CuCO, 113779-79-6; $L_{OBu}$CuCO, 113779-80-9; $L_{Et}$CuCO, 113779-81-0; $L_{Pr}$CuCO, 113779-82-1; $L_{Bu}$CuCO, 113779-83-2; $L_{OMe,Me}$CuCO (isomer 1), 113779-84-3; $L_{OMe,Me}$CuCO (isomer 2), 113889-54-6; $L_{OMe,Et}$CuCO (isomer 1), 113779-85-4; $L_{OMe,Et}$CuCO (isomer 2), 113830-32-3; $L_{OMe,Ph}$CuCO (isomer 1), 113779-86-5; $L_{OMe,Ph}$CuCO (isomer 2), 113830-33-4; $L_{O\text{-}i\text{-}Bu,Me}$CuCO (isomer 1), 113779-87-6; $L_{O\text{-}i\text{-}Bu,Me}$CuCO (isomer 2), 113830-34-5; L*$_{OMe}$CuCO, 113779-88-7; L*$_{OEt}$CuCO, 113779-89-8; $L_{O\text{-}i\text{-}Pr}$Cu(C$_2$H$_4$), 113779-92-3; $L_{OEt}$Cu(C$_2$H$_4$), 113779-93-4; $L_{OMe}$Cu(MA), 113779-94-5; $L_{O\text{-}i\text{-}Pr}$Cu(MA), 113779-95-6; Na$L_{OMe}$, 82149-18-6; Na$L_{OMe,Me}$, 113779-70-7; Na$L_{OMe,Et}$, 113779-71-8; Na$L_{OMe,Ph}$, 113779-72-9; Na$L_{O\text{-}i\text{-}Bu,Me}$, 113779-73-0; NaL*$_{OMe}$, 113779-74-1; Na$L_{OEt}$, 70850-86-1; Na$L_{O\text{-}i\text{-}Pr}$, 110935-74-5; Na$L_{OBu}$, 110935-73-4; Na$L_{Et}$,

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87965-88-6; $NaL_{Pr}$, 113779-90-1; $NaL_{Bu}$, 113779-91-2; $NaL^{*}_{OEt}$, 106333-06-6; $Na[(C_5H_5)Co\{P(O)(OMe)_2\}(CN)_2]$, 113779-75-2; $Na_3[Co(CN)_6]$, 14039-23-7; $[Cu(CH_3CN)_4]PF_6$, 64443-05-6; $CuSO_4$, 17599-81-4; $C_2H_4$, 74-85-1; Cu, 7440-50-8; methylphosphonous acid monomethyl ester, 14402-47-2; ethylphosphonous acid monomethyl ester, 27852-48-8; phenylphosphonous acid monomethyl ester, 63581-54-4; methylphosphonous acid monoisobutyl ester, 27852-51-3.

**Supplementary Material Available:** A listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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# Reactivity and Mechanism in Oxidative Addition to Palladium(II) and Reductive Elimination from Palladium(IV) and an Estimate of the Palladium–Methyl Bond Energy

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Oxidative addition of MeI to $[PdMe_2(bpy)]$ (bpy = 2,2′-bipyridine) occurs by the $S_N2$ mechanism. Evidence includes the observation of second-order kinetics in acetone solvent, with a large negative value for the entropy of activation, and the observation of a cationic species, $[PdMe_3(bpy)(CD_3CN)]^+I^-$, in $CD_3CN$ solvent. The reaction occurs more slowly than the analogous reaction of $[PtMe_2(bpy)]$, but the same mechanism operates. Reductive elimination from $[PdIMe_3(bpy)]$ to give ethane and $[PdIMe(bpy)]$ follows good first-order kinetics, occurs more rapidly in polar solvents, and is strongly retarded by added iodide. These observations are interpreted in terms of a mechanism that involves preliminary ionization of iodide followed by reductive elimination from the cation $[PdMe_3(bpy)]^+$. Studies by differential scanning calorimetry allow an estimate of the Pd–C bond energy of ~130 kJ $mol^{-1}$ to be obtained, and this value is considerably higher than the activation energy for reductive elimination of ethane from $[PdIMe_3(bpy)]$. The reductive elimination step is therefore concerted, and possible mechanisms, which may involve direct C–C coupling or C–C coupling after an agostic CHPd interaction, are discussed. This work is relevant to catalytic C–C coupling reactions using palladium complex catalysts.

## Introduction

The catalysis by palladium complexes of the coupling reaction of organometals RM and organohalides R′X to give RR′ and MX is thought to be possible by oxidative addition–reductive elimination cycles involving either Pd(0)–Pd(II) or Pd(II)–Pd(IV) complexes.[2] Models for the former catalytic cycle have been developed,[3] but this has not been possible with Pd(II)–Pd(IV) systems since the proposed organopalladium(IV) intermediates could not be detected by spectroscopic methods.[4-7] The recent discovery of oxidative addition of methyl iodide to $[PdMe_2(bpy)]$ (1) to give $[PdIMe_3(bpy)]$ (2) which only slowly undergoes reductive elimination of ethane to give $[PdIMe(bpy)]$ (3) (bpy = 2,2′-bipyridine) allows a study of the mechanisms of the reactions.[8-10]

## Results

**The Oxidative Addition Reaction.** The reaction of $[PdMe_2(bpy)]$ with MeI in $CD_3CN$ was monitored by $^1H$ NMR. The reagents were mixed at −40 °C, and at this temperature resonances due to two products in ~3:1 ratio were observed. Resonances due to the major product $[PdIMe_3(bpy)]$ were at $\delta$ 1.79 (PdMe trans to N) and 1.20 (PdMe trans to I); the second product was assigned to the ionic $[PdMe_3(CD_3CN)(bpy)]^+I^-$ with $\delta$ 1.61 (PdMe trans to bpy) and 1.06 (PdMe trans to $CD_3CN$), related to isolated cations involving tripodal nitrogen donor ligands such as $[PdMe_3\{tris(pyridin\text{-}2\text{-}yl)methane\}]I$.[9] Methyl group resonances for the cation broaden on warming, with coalescence at ≥−5 °C, but bpy resonances for the cation and all resonances for $[PdIMe_3(bpy)]$ remain sharp, consistent with intramolecular exchange (scrambling) of methyl environments in the cation; on recooling to low temperature the original spectrum is obtained, with identical integration. At higher temperatures (≥15 °C) bpy resonances for the neutral and cationic complexes are coalesced, and the bpy and methyl resonances are broad compared to the sharp, growing resonances for the product $[PdIMe(bpy)]$, indicating exchange between $[PdMe_3(bpy)(CD_3CN)]^+I^-$

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