purchase of the mass spectrometer system.

Registry No. $Co(C_7H_{11})_2BF_4$, 91228-14-7; $[Co(C_7H_{11})_2]_2$, 91208-79-6; cobaltous chloride, 7646-79-9.

Supplementary Material Available: A listing of atomic parameters (Table I) and the structure amplitude table (6 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of a Mononuclear Copper(I) Complex Containing the Copper(I) σ-Phenyl Functionality

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Summary: Reaction of [(triphos)CuCl] [triphos = 1,1,1-tris[(diphenylphosphino)methyl]ethane, $MeC(CH_2PPh_2)_3$] with lithium phenyl in tetrahydrofuran afforded the mononuclear complex [(triphos)CuPh], containing a phenyl group σ bonded to copper(I) with a Cu-C bond distance of 2.020 (4) Å. Copper(I) is in a pseudotetrahedral geometry provided by the triphos ligand and the phenyl group.

Copper(I) alkyl or copper(I) aryl is one of the most interesting organometallic functionalities.[1,2] Its chemistry, however, has to be related to either the bonding mode of the carbon donor ligand or the nature of the ancillary ligands around the metal.[1] This relationship, however, has not been established because of the lack of structural information available.[1,2] Carbon donor ligands are normally engaged in multinuclear structures, where they display a two-electron, three-center bonding mode.[2,3] In such compounds the carbon donor ligand has never been structurally found to display a terminal bonding mode, like that expected in the model L_nCu-Ar (L_n = ancillary ligands) compound, except for a recent reported dimesitylcuprate(I) derivative.[4] The bonding mode of an anionic ligand is, however, always changing from a neutral to a cuprate(I)-type complex[5] and its reactivity, too.[1]

The tridentate tripod-like ligand 1,1,1-tris[(diphenylphosphino)methyl]ethane, $[MeC(CH_2PPh_2)_3]$, triphos, provides the appropriate coordination sphere around copper(I) in order to force the fourth ligand to display a terminal bonding mode.[6] Using triphos as the ancillary ligand, we achieved the stabilization of the first monomeric phenylcopper complex.

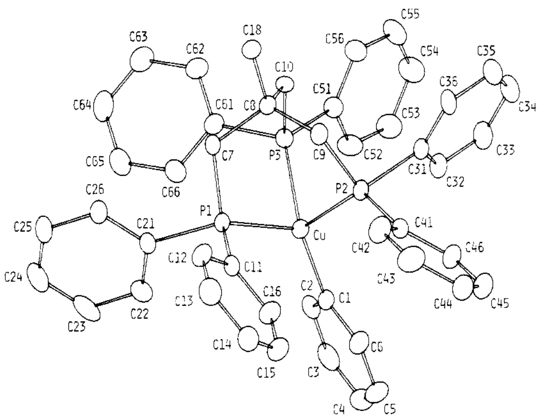
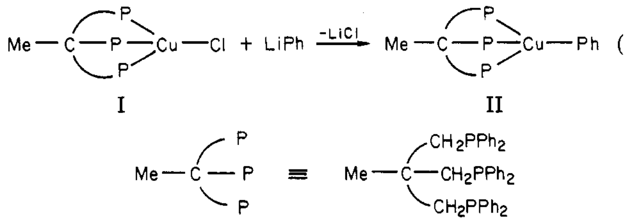


Figure 1. ORTEP drawing of complex II [(triphos)CuPh] (30% probability ellipsoids). Bond distances (Å): Cu-P1 = 2.342 (2), Cu-P2 = 2.276 (2), Cu-P3 = 2.295 (2), and Cu-C1 = 2.020 (4). Bond angles (deg): P3-Cu-C1 = 124.8 (1), P2-Cu-C1 = 126.9 (1), P1-Cu-C1 = 119.4 (1), P2-Cu-P3 = 93.3 (1), P1-Cu-P3 = 91.9 (1), and P1-Cu-P2 = 90.9 (1).

Copper(I) chloride (1 mol) was dissolved in a THF solution of *N,N,N′,N′*-tetramethylethylenediamine (1 mol) and then the mixture reacted with triphos. The solution on standing gave white crystals of [(triphos)CuCl][7,8] (I). This procedure must be used in order to obtain I as a crystalline solid suitable for an X-ray analysis.[8] The structure of I is suggested on the basis of preliminary results from an X-ray study.

A THF suspension of I was reacted with an equimolar amount of LiPh in THF. The bright yellow solution was concentrated, followed by addition of Et_2O. The final solution gave on standing for 24 h crystals of II (ca. 60%).[9]



$$\text{Me}-\text{C}(\text{P})_3\text{Cu}-\text{Cl} + \text{LiPh} \xrightarrow{-\text{LiCl}} \text{Me}-\text{C}(\text{P})_3\text{Cu}-\text{Ph} \quad (1)$$

I II

$$\text{Me}-\text{C}(\text{P})_3 \equiv \text{Me}-\text{C}(\text{CH}_2\text{PPh}_2)_3$$

It is difficult to define the influence that the phosphorous donor ligands can have on the stability of copper-carbon bond, very significant differences being observed with bidentate[10] or monodentate[11] phosphines. An important distinction must be made, however, on whether the synthesis of (phosphine)alkyl- or (phosphine)arylcopper(I) complexes is carried out by the reaction of phosphine ligands with the preformed copper(I) organometallic species or by the alkylation of the corresponding phosphine halo complexes. Crystallographic details for complexes II are as follows: $C_{47}H_{44}CuP_3$, orthorhombic, space group $Pna2_1$ (from systematic absences and structural analysis),

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a = 18.382 (3) Å, b = 12.589 (2) Å, c = 17.154 (3) Å, V = 3970 (1) Å^3, Z = 4, D_{calcd} = 1.28 g cm^{-3}, Cu Kα radiation (λ = 1.54178 Å), μ(Cu Kα) = 21.5 cm^{-1}. The structure was solved by the heavy-atom method and refined anisotropically by full-matrix least squares. All the hydrogen atoms were located from difference Fourier syntheses and introduced as fixed contributors in the least-squares refinement (U = 0.05 Å^2). For 2535 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on a Siemens AED diffractometer in the range $6 < 2\theta < 120°$ the current R is 0.037 (R_w = 0.041). No absorption correction was applied.

The structure of [$\mathrm{MeC(CH_2PPh_2)_3Cu(Ph)}$] (Figure 1) consists of monomeric unit whose coordination geometry is that of a distorted tetrahedron defined by three phosphorus atoms from triphos ligand and a carbon atom from the phenyl ring. The angles at the copper atom are far from the expected tetrahedral geometry, the C–Cu–P and P–Cu–P angles ranging from 119.4 (1) to 126.9 (1)° and from 90.0 (1) to 93.3 (1)°, respectively, as a consequence of the strain of the chelating phosphine ligand. The Cu–P distances [2.342 (2), 2.276 (2), 2.295 (2) Å], which are within the range observed for four-coordinate copper(I) phosphine complexes,[6,12] differ significantly from each other. This is, probably, the consequence of steric interactions between the chelating ligand and the σ-bonded phenyl group. As a matter of fact, this structure can be compared with that of complex I, [(triphos)CuCl],[8] where the steric hindrance between the coordinate ligands is released by the substitution of phenyl with chlorine and the three Cu–P distances are not significantly different from each other [ranging from 2.300 (5) to 2.285 (5) Å].[8] The copper atom lies nearly in the plane of the coordinate phenyl ring [0.033 (1) Å out of it].

The terminal bonding mode of the phenyl group does not affect the Cu–C bond distance [2.020 (4) Å] that is very close to those in polynuclear aggregates where the phenyl group acts as a bridging ligand between two copper atoms.[8] The reactivity of a single copper–carbon σ bond was so far prevented because of the complex structure in which the organic residue is usually engaged.[2] The reactivity of the copper–carbon bond in complexes like II is being investigated.

Acknowledgment. This work was supported by CNR (Rome).

Supplementary Material Available: Listings of observed and calculated structure factors, fractional atomic coordinates, thermal parameters, and bond distances and angles for complex II (13 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of (Arene)manganese Dicarbonyl Halides and Hydride

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Summary: Compounds I, η^6-ArMn(CO)$_2$X (X = Cl, Br, I), prepared via the photolysis of the corresponding (arene)manganese tricarbonyl cations in the presence of halide ion, have been characterized by mass, NMR, and IR spectroscopy and elemental analysis. The hydride η^6-ArMn(CO)$_2$H, II (Ar = hexamethylbenzene), was prepared by NaBH$_4$ reduction of Ia and characterized by mass, NMR, and IR spectroscopy.

Previous reports of η^6-ArMn(CO)$_2$Y, synthesized from the tricarbonyl cations, include Y = CN,[1] alkyl,[2] aryl,[2] acyl,[2] C(O)NHR,[3] and C(O)OR.[4] These species are of interest because they represent a class of compounds that are isoelectronic analogues of CpFe(CO)$_2$Y. The synthetic accessibility of various η^6-ArMn(CO)$_2$Y derivatives, thus far limited to the chemistry of η^6-ArMn(CO)$_3^+$, should be enhanced by the availability of η^6-ArMn(CO)$_2$X (X = halide), I. These species would be expected to display nucleophilic substitution reactions similar to those used to synthesize a wide range of derivatives of the iron analogues. We wish to report the synthesis, characterization, and some initial reactivity studies of compounds I. Our approach to the synthesis of these compounds, patterned after the method used by Sweigart[5] et al. in the synthesis of η^6-ArMn(CO)$_2$PR$_3^+$, is shown in eq 1. Our preliminary

$$\mathrm{ArMn(CO)_3^+ + NaX \xrightarrow{h\nu} ArMn(CO)_2X} \qquad (1)$$

Ia, Ar = η^6-C$_6$Me$_6$ (HMB), X = I
Ib, Ar = η^6-C$_6$Me$_6$ (HMB), X = Br
Ic, Ar = η^6-C$_6$Me$_6$(HMB), X = Cl
Id, Ar = η^6-C$_6$H$_3$Me$_3$ (MES), X = I

nucleophilic substitution studies are limited to derivatives of the arene hexamethylbenzene (HMB) in order to minimize the formation of products arising from nucleophilic attack at the aromatic ring.[6]

The compounds I were synthesized from η^6-ArMn(CO)$_3^+$X^{-}[7] via photolysis, with a 350-nm source, in a homogeneous aqueous solution of the appropriate sodium halide. The photolyses, which required 3–5 h for optimum yields,[8] resulted in the formation of red solids that were isolated by filtration and purified by column chromatography on silica with hexane/acetone as an eluent. Compounds I, which are all crystalline solids, vary in color from deep purple, for the iodide, to bright red for the chloride. When heated they undergo relatively sharp transitions[9] with loss of a white crystalline solid that has the melting point of hexamethylbenzene (163 °C). No attempt has been made to characterize the residue from this thermal decomposition.

Compounds Ia–c were characterized by IR, NMR, and mass spectroscopy and elemental analysis (Table I, ref 10 and 11). Id was characterized by spectroscopic comparison with Ia–c. Consistent with the observation for the iron

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[7] When X$^-$ is PF$_6^-$, low yields are obtained but use of the hydrolysate, obtained in the aqueous workup of the solid product from the cation preparation, presumably η^6-C$_6$Me$_6$Mn(CO)$_3^+$AlCl$_3$Br$^-$, gives the yields reported herein.

[8] Compound/yield: Ia/76%, Ib/64%, Ic/19%, Id/not isolated, and II/80%.

[9] Compound/mp: Ia/135–138 °C, Ib/125–126 °C, Ic/114–115 °C, and II/120–130 °C.

[10] Mass spectral data [compound (m/z/ion)]: Ib (298, 296/HMBMnBr$^+$), (217/HMBMn$^+$), (162/HMB$^+$); Ic (273/HMBMn(CO)$_2^+$), (254, 252/HMBMnCl$^+$), (245/HMBMnCO$^+$), (217/HMBMn$^+$), (162/HMB$^+$); II (274/HMBMn(CO)$_2$H), (273/HMBMn(CO)$_2^+$), (245/HMBMnCO$^+$), (218/HMBMnH$^+$), (217/HMBMn$^+$), (162/HMB$^+$).

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