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 [MeC(CH$_2$PPh$_2$)$_3$Cu(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.

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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

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

$$\begin{array}{l}\text{Ia, Ar} = \eta^6\text{-C}_6\text{Me}_6\text{ (HMB), X = I}\\ \text{Ib, Ar} = \eta^6\text{-C}_6\text{Me}_6\text{ (HMB), X = Br}\\ \text{Ic, Ar} = \eta^6\text{-C}_6\text{Me}_6\text{(HMB), X = Cl}\\ \text{Id, Ar} = \eta^6\text{-C}_6\text{H}_3\text{Me}_3\text{ (MES), X = I}\end{array}$$

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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Table I. ^{1}H NMR[a] and IR[b] Data

compd	^{1}H NMR, ppm	IR ν(CO), cm^{-1}
Ia	2.36 (s)	1968, 1920[c]
Ib	2.25 (s)	1971, 1921[c]
Ic	2.25 (s)	1972, 1920[c]
Id	2.43 (s) [9 H],[d] 5.1 (s) [3 H]	1981, 1973[e]
II	2.35 (s) [18 H], −10.9 (s) [1 H][e]	1945, 1890[e]

[a] In $CDCl_3$. [b] All absorption bands are strong. [c] Acetone. [d] Relative number of protons. [e] Dichloromethane.

analogues, the carbonyl stretching frequencies of compounds Ia–d are lower than their corresponding tricarbonyl cations. The ^{1}H NMR spectra for compounds Ia–c (Table I) all consist of a singlet between 2.25 and 2.36 ppm. Compound Id shows two singlets as expected for coordinated mesitylene (MES) with the aromatic ring protons shifted upfield by 1.60 ppm relative to uncoordinated mesitylene.[12] The proton-decoupled ^{13}C NMR spectrum of Ia reveals three singlets: 228.6 (Mn–CO), 104.0 (Mn–*C*–C), and 16.75 ppm (Mn–C–*C*). The nondecoupled spectrum shows the resonance at 16.75 ppm splits into a quartet as expected for the proposed structure. Mass spectral data for Ia show a parent ion at *m/z* 400 and ions at *m/z* 344 and 217 as expected for the parent minus two carbonyls and the parent minus two carbonyls and an iodide, respectively. The mass spectra of Ib and Ic show no parent ions but display ions consistent with decomposition pathways predicted for compounds I.[10]

Compound II, a yellow solid, was synthesized from Ia in THF, at 50 °C, with an excess of $NaBH_4$ (eq 2). The

$$\text{Ia} + NaBH_4 \rightarrow \underset{\text{II}}{(HMB)Mn(CO)_2H} \qquad (2)$$

reduction required 2–5 h and was monitored by change in the CO stretching frequency of the IR spectrum. It was isolated by vacuum sublimation from the solid residue left by vacuum evaporation of the solvent. This new compound, to our knowledge, the first reported isolable (η^6-arene)metal carbonyl hydride, has been characterized by mass, ^{1}H NMR, and IR spectroscopy and elemental analysis (Table I, ref 10 and 11). The chemical shift of the Mn–*H*, (CH_2Cl_2) −10.9 ppm, is comparable to that of $(\eta^5\text{-}C_5(CH_3)_5)Fe(CO)_2H$[13] and is characteristic of transition-metal hydrides. Like compounds I, when heated, II undergoes a transition from 120 to 130 °C with loss of a white crystalline solid that melts at 163 °C. The lack of bimolecular elimination of H_2 from II up to 120 °C is consistent with the behavior of $(\eta^5\text{-}C_5(CH_3)_5)Fe(CO)_2H$, which is reported to be thermally stable.[14] In contrast to the instability of $CpFe(CO)_2H$,[15] which decomposes giving H_2 at 20 °C, the stability of both of these compounds may be due to the steric hindrance of bimolecular interaction accompanying permethylation of the π ligands.

Compound Ib reacts with NaCN in refluxing methanol to yield, quantitatively by IR, η^6-ArMn(CO)$_2$CN, III (eq 3).[16] The melting point, IR, and ^{1}H NMR all agree with

$$\text{Ib} + NaCN \rightarrow \underset{\text{III}}{(HMB)Mn(CO)_2CN} \qquad (3)$$

literature values.[1] Ib also reacts with MeLi, at −78 °C in THF, to quantitatively yield the previously reported η^6-ArMn(CO)$_2$Me, IV (eq 4).[16] The spectroscopic characteristics (IR and NMR) match the literature reported values.[2] The three reactions summarized in eq 2–4 show the synthetic utility of compounds I with respect to nucleophilic displacement of the halide. This reactivity corresponds directly to that displayed by the isoelectronic $CpFe(CO)_2X$ analogues.[17]

$$\text{Ib} + MeLi \rightarrow \underset{\text{IV}}{(HMB)Mn(CO)_2Me} \qquad (4)$$

We are currently in the process of exploring the synthetic utility of this new series of halides as well as the hydride. In addition an X-ray crystallographic study of Ic is in progress.

Registry No. Ia, 91230-49-8; Ib, 91230-50-1; Ic, 91230-51-2; Id, 91230-52-3; II, 91230-53-4; III, 41638-97-5; IV, 65643-58-5; (HBM)Mn(CO)$_3$$^+$AlCl$_3Br^-$, 91230-54-5; (MES)Mn(CO)$_3$$^+$AlCl$_3Br^-$, 91238-35-6.

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[11] Anal. Calcd for Ia: C, 42.02; H, 4.53. Found: C, 41.45; H, 4.54. Anal. Calcd for Ib: C, 47.62; H, 5.14. Found: C, 47.24; H, 5.06. Anal. Calcd for Ic: C, 54.47; H, 5.88. Found: C, 54.05; H, 5.61. Anal. Calcd for II: C, 61.32; H, 6.99. Found: C, 61.23; H, 7.11.

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Diastereomeric Equilibria and Barrier of Rotation in Cationic Iron Diphosphine Alkylidenecarbene (Vinylidene) Complexes

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Summary: In the preferred geometry for $[(\eta\text{-}C_5H_5)Fe(\text{diphosphine})(C{=}CHR)]PF_6$ complexes the plane of the alkylidenecarbene ligand is not perpendicular to that of the cyclopentadienyl ligand; barriers for rotation have been evaluated to be 9–10 kcal/mol through ^{31}P NMR spectroscopy. The equilibrium composition of the two diastereomeric conformers for complexes containing the 2,3-butanediylbis(diphenylphosphine) ligand is influenced by the bulkiness of the substituent on the alkylidenecarbene moiety (C_6H_5 vs. CH_3); when *trans*-1,2-cyclopentanediylbis(diphenylphosphine) is the ligand, only one rotamer is recognizable in the low-temperature spectra for R = methyl, *tert*-butyl, and phenyl.