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Notes

Synthesis and Characterization of the First Pentaphenylcyclopentadienyl Copper(I) Complex, $(Ph_5Cp)Cu(PPh_3)$

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*Summary: $(Ph_5Cp)Cu(PPh_3)$ (**1**) has been synthesized from $Na[Ph_5Cp]$ and $[(PPh_3)CuCl]_4$. Complex **1** is the first reported pentaphenylcyclopentadienyl−copper complex and is a rare example of a π-bound Cu−Cp complex. Complex **1** has been fully characterized, including crystallographically; the ^{31}P NMR chemical shift for the triphenylphosphine ligand in **1** appears unusually far downfield for a Cu(I)−PPh_3 complex, at +23.2 ppm.*

Introduction

Cyclopentadienyl (Cp) and substituted cyclopentadienyl ligands are prevalent in the organometallic chemistry of the transition metals. For copper, however, only a handful of π-bound Cp complexes have been structurally characterized.[1−6] The limited number of Cu−Cp complexes is due, at least in part, to a weaker η^5-Cp bonding interaction for copper than is found for most other transition metals. Consistent with that postulation is the observation that many copper−cyclopentadienyl complexes are reported to easily lose the Cp ligand,[7−9] including the fast reaction of $CpCu(PEt_3)$ with $FeCl_2$ to form ferrocene.[10] Here we report the synthesis and characterization of a rare example of this class of compounds, $(Ph_5Cp)Cu(PPh_3)$ (**1**), adding to our studies of aromatic π-ligated copper(I) complexes.[11] Complex **1** is the first copper complex with the pentaphenylcyclopentadienyl ligand.

The preparations of Ph_5Cp ligand precursors were initially reported in 1925[12] and have since been the subject of several modifications and additions.[13−19] Although nearly 40 years lapsed before the first $[Ph_5Cp]^-$ complex was described,[20] since that time numerous studies utilizing a variety of metals have appeared.[21−26] Sometimes very different and/or unusual properties have been found for Ph_5Cp-ligated complexes as compared to the analogous Cp or alkyl-substituted Cp complexes. This is, of course, due to the combination

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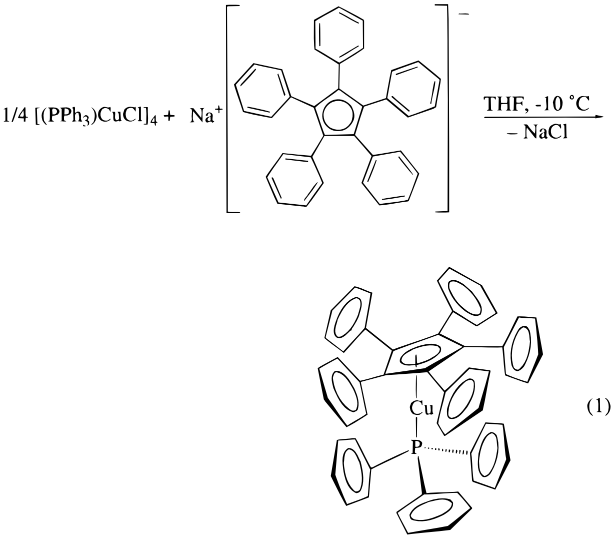
of the increased steric bulk as well as the electron-withdrawing nature that the phenyl groups impart to the system.[27]

Results and Discussion

The ligand was synthesized by a combination of literature methods.[28] First, tetraphenylcyclopentadienone was synthesized from benzil and 1,3-diphenylacetone by the procedure of Johnson and Grummitt.[29] The fifth phenyl ring was added via a Grignard reaction, similar to the method reported by Chambers et al.[15] The resulting alcohol was reduced to pentaphenylcyclopentadiene with lithium aluminum hydride, as also used in the last half of Beletskaya's one-pot procedure.[19] Finally, pentaphenylcyclopentadiene was deprotonated with NaH to form the pentaphenylcyclopentadienyl anion.[30] We did not isolate Na[Ph_5Cp]; instead we generated it as a fresh solution and used that solution directly in the synthesis of **1**.

Under a nitrogen atmosphere, a nearly stoichiometric mixture of Na[Ph_5Cp] and [(PPh_3)CuCl]$_4$[31] in THF was stirred for 6 h at −10 °C (eq 1). This method is similar to that used to synthesize Cp^*CuPPh_3.[32] After washing the crude compound with Et_2O and removing benzene-insoluble side products, crystallization was achieved by the slow addition of Et_2O into a THF solution of **1**. The colorless needles were isolated in almost 40% yield, which was not optimized. Single, nearly cubic crystals were grown by the slow diffusion of Et_2O into a CH_2Cl_2 solution of **1**. Complex **1** is somewhat air-sensitive in solution, for example turning green over a day or so in CH_2Cl_2, but remains colorless as a solid open to the air for at least several days.



(1)

1

Complex **1** has been characterized by ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopies, FAB-MS, elemental analysis, and X-ray crystallography. The proton NMR spectrum is fairly uninformative due to the presence of only aromatic signals that extensively overlap. The $^{13}C\{^{1}H\}$ spectrum is consistent with the assignment of **1**, including phosphorus coupling to the *ipso*, *ortho*, and *meta* carbon phenyl resonances from the PPh_3 ligand. On the other hand, the $^{31}P\{^{1}H\}$ NMR is quite simple, with a single resonance for **1** appearing at 23.2 ppm downfield from H_3PO_4: a remarkable $\Delta\delta$ of 28.8 ppm versus free PPh_3 (−5.6 ppm). Although it is typical for the ^{31}P NMR signal for PPh_3 to move downfield upon coordination to the copper(I) ion, the magnitude of the shift is usually

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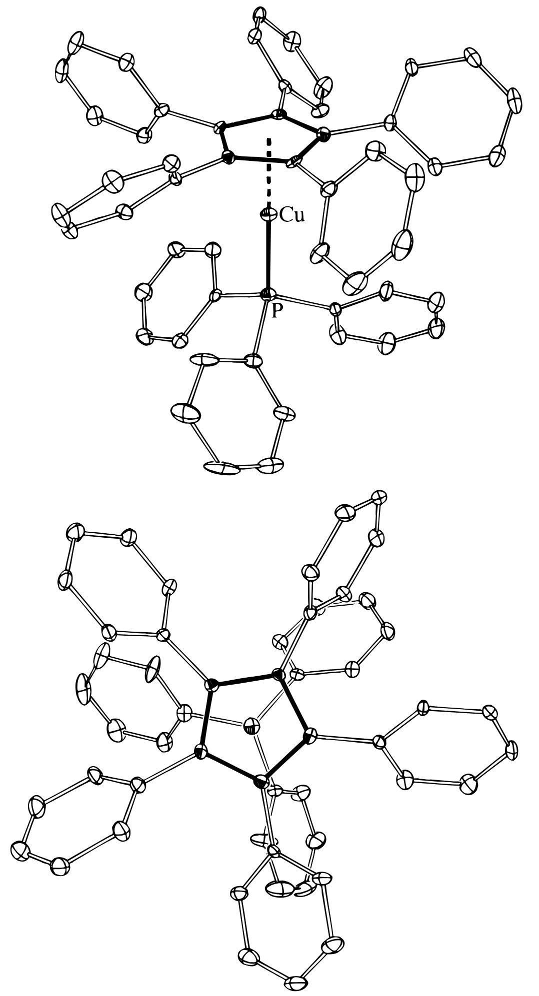

Figure 1. Thermal ellipsoid depictions of **1** at the 10% probability level, viewed from the side (above) and down the Cu−P vector (below) with hydrogens omitted for clarity.

less than 15 ppm.[33] Thus, **1** displays an unusual chemical shift for a copper(I)−PPh_3 complex, undoubtedly due to the influence of the phenyl groups from the Ph_5Cp ligand. The FAB$^+$ mass spectrum of **1** contained a weak molecular ion and the ligand-derived peak [Ph_5CpH^+], which has been observed in other Ph_5Cp systems.[21d,22d,e,23l,24c]

Complex **1** crystallized in the chiral space group $P2_12_12_1$; the molecule is chiral because of the propeller-like Ph_5Cp ligand (Figure 1). The copper is bound to the Ph_5Cp ligand in an η^5-fashion, with a distorted tetrahedral geometry about the Cu(I) ion if the Ph_5Cp ligand is considered three-coordinate. Alternatively, if the Ph_5Cp ligand is considered to occupy a single coordination site, the copper geometry is almost linear; in fact, the $Cp_{centroid}$−Cu−P angle is 179.1°. The remaining important metrical data for complex **1** are in good agreement with the three other Cp and substituted-Cp copper−phosphine complexes (Table 1), reflecting an apparent indifference to the nature of the phosphine (alkyl or aryl) or cyclopentadienyl (Cp, MeCp, or Ph_5Cp) ligands. For example, the Cu−P distance in **1** is 2.126(3) Å and in the other three complexes ranges from 2.131(1) to 2.136(9) Å. The only noteworthy difference is in the $Cp_{centroid}$−Cu−P angles, which vary from 173.1° to 179.9°, most likely a consequence of packing forces.

Table 1. Selected Bond Distances and Angles for 1 and Other $CpCuPR_3$ Complexes

	(Ph_5Cp)Cu-(PPh_3) (**1**)	CpCu-(PPh_3)	CpCu-(PEt_3)	(MeCp)Cu-(PPh_3)
Cu−P	2.126(3) Å	2.135(1) Å	2.136(9) Å	2.131(1) Å
Cu−$Cp_{centriod}$	1.876 Å	1.864 Å	1.90 Å	1.865 Å
average Cu−C	2.234(10) Å	2.211(3) Å	2.238(26) Å	2.214(6) Å
average C−C	1.430(12) Å	1.399(4) Å	1.381(35) Å	1.402(9) Å
$Cp_{centroid}$−Cu−P	179.1°	175.2°	179.9°	173.1°
reference	this work	1	2	4

In conclusion, the new copper−cyclopentadienyl complex **1** has been synthesized and characterized. The X-ray crystal structure for **1** is one of only a few determined for this limited class of compounds, but is otherwise unexceptional. A most intriguing observation noted for **1** is its phosphorus NMR signal, which appears unusually far downfield for a copper(I)−triphenylphosphine complex.

Experimental Section

All reagents were used as received from Acros, Aldrich, EM, Fisher, or Spectrum, except bromobenzene, which was washed with aqueous acid and base and dried over Na_2SO_4.[34] Solvents were dried and freshly distilled from the following drying agents: benzene and dichloromethane from calcium hydride; diethyl ether and tetrahydrofuran from sodium metal. Pentaphenylcyclopentadienol, sodium pentaphenylcyclopentadienide, and **1** were synthesized using standard Schlenk techniques. ^1H NMR spectra were recorded on a General Electric QE 300 MHz FT-NMR spectrometer; ^{31}P and ^{13}C NMR spectra were recorded on a Varian Unity 500 MHz spectrometer. ^1H NMR and ^{13}C NMR spectra were referenced to the resonance of the solvent $CDCl_3$ (^1H, δ 7.27; ^{13}C, δ 77.23), and ^{31}P NMR spectra were referenced to the resonance of triphenylphosphine (−5.6 ppm), which served as a secondary standard referenced to aqueous H_3PO_4 at 0.0 ppm. Infrared spectra were recorded on a Perkin-Elmer model PARAGON 1000 PC FT-IR spectrophotometer. The FAB/MS was done by the University of California, Riverside Mass Spectrometry Facility, on their VG ZAB mass spectrometer in a DCM/NBA matrix. The elemental analysis was performed by NuMega Resonance Labs (San Diego, CA). The melting point was determined in an open glass capillary on a Thomas-Hoover model 6406-H melting-point apparatus and is uncorrected.

X-ray Diffraction Measurements. An approximately cubic colorless crystal of dimensions 0.36 × 0.34 × 0.34 mm was mounted with silicone caulk to a glass fiber on the bench top, and the data were collected with a Siemens P4 diffractometer using Mo Kα radiation (λ = 0.710 73 Å) at ambient temperatures. The structure was solved (Patterson direct methods) and refined with the Siemens SHELXTL version 5.0.3 PC software package. All non-hydrogen atoms were modeled anisotropically. Hydrogens were placed at calculated distances and use a riding model, where the positional and thermal parameters are derived from the carbon atom each hydrogen is bound to, while maintaining the calculated distance and optimal angles. Crystallographic data: $C_{53}H_{40}$-CuP, orthorhombic, $P2_12_12_1$, a = 10.3409(7) Å, b = 19.183(2)

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Å, $c = 20.824(2)$ Å, $Z = 4$, $R1 = 0.0563$ ($wR2 = 0.1106$), goodness of fit on $F^2 = 1.012$.

(Pentaphenylcyclopentadienyl)(triphenylphosphine)-copper(I) (1). A solution of $NaPh_5Cp$, made from Ph_5CpH, 1.02 g (2.3 mmol), and NaH, 97 mg (4.0 mmol), in 20 mL of THF, was added to a flask containing $(ClCuPPh_3)_4$[31] (0.72 g, 0.50 mmol) in 15 mL of THF. The resulting solution was cooled to −10 °C and stirred for 6 h. The solution was then allowed to slowly warm to room temperature and the solvent was removed in vacuo, leaving a yellow to brown solid. The solids were washed with diethyl ether (50 mL), and the benzene-insoluble impurities were removed by addition of 80 mL of benzene followed by filtration. The benzene was distilled away, and the resulting solids were dissolved in 15 mL of THF. Complex **1** was crystallized by slow diffusion of diethyl ether (50 mL) into the THF solution, forming colorless needlelike crystals overnight. Yield: 679 mg (0.88 mmol, 39%). Two subsequent recrystallizations of **1** from THF/Et_2O gave analytically pure compound. ^1H NMR: δ 6.9-7.0 (m, 25 aromatic *H*); 7.3-7.4 (m, 15 aromatic *H*). $^{13}C\{^1H\}$ NMR: δ 113.4 (5 C, C_5Ph_5); 124.5 (5 C, Cp-(*para-C*)$_5$); 127.0 (10 C, Cp-(*meta-C*)$_5$); 128.8 (6 C, d, $^3J_{P-C} = 10.6$ Hz, P-(*meta-C*)$_3$); 130.6 (3 C, P-(*para-C*)$_3$); 131.7 (3 C, d, $^1J_{P-C} = 45.4$ Hz, P-(*ipso-C*)$_3$); 132.3 (10 C, Cp-(*ortho-C*)$_5$); 133.6 (6 C, d, $^2J_{P-C} = 15.3$ Hz, P-(*ortho-C*)$_3$); 136.8 (5 C, Cp-(*ipso-C*)$_5$). $^{31}P\{^1H\}$ NMR: δ 23.2 ppm. IR (KBr): 3052 ms; 1948 w; 1881 w; 1809 w; 1596 s; 1575 m; 1501 s; 1480 ms; 1436 s; 1328 w; 1308 w; 1262 w; 1181 m; 1154 m; 1138 ms; 1098 s; 1073 s; 1027 s; 999 m; 914 m; 848 w; 805 ms; 778 s; 741 s; 697 vs; 618 mw; 550 ms; 536 s; 497 s. FAB/MS: $m/z = 770/772$ [M^+] (5%), 446 [Ph_5CpH^+] (100%). Anal. Calcd for $C_{53}H_{40}CuP$: C, 82.52; H, 5.23. Found: C, 82.40; H, 4.92. Mp: 156 °C (dec).

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Supporting Information Available: Crystallographic tables for **1**, including atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, bond lengths and bond angles, and calculated positions for hydrogen atoms (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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