Table II

Molecule	Charge on Pt Mulliken	Löwdin
$(PH_3)_2Pt(CH_3C{\equiv}C{-}CH_3)$	+1.579	−0.077
$(PH_3)_2Pt(CH_3C{\equiv}C{-}H)$	+1.537	−0.067
$(PH_3)_2Pt(C_2H_4)$	+1.585	−0.044
$(PH_3)_2Pt(TCNE)$	+2.172	+0.094

acetylenes separately, as the charge density is a function of both σ and π effects. Calculations are currently in progress to assess the relative bonding contributions of olefins and acetylenes.

The magnitude of the calculated energy barriers for the zerovalent complexes suggests that it might be possible to observe rotation in the nmr spectra at elevated temperatures. The spectra must, however, be obtained in solvents which do not react with the complexes, therefore precluding halocarbon solvents such as chloroform, with which the following oxidative addition reaction is known to occur[13]

$$L_2Pt(Ac) + XY \longrightarrow L_2XPtY + Ac$$

where L = triphenylphosphine, Ac = acetylene, X = halogen, and Y = the hydrocarbon or halocarbon fragment. Preliminary thermodynamic investigations indicate that the oxidative addition reactions occur before rotation can be observed in these solvents.[47]

Acknowledgments. We wish to acknowledge the financial support of the Esso Research Laboratories, Humble Oil and Refining Company, Baton Rouge, La.

[47] J. H. Nelson and H. B. Jonassen, unpublished results.

Systematic Preparation and Characterization of *Pentahapto*cyclopentadienylcopper(I) Compounds[1]

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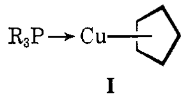
Abstract: A convenient and general method for the preparation of $(h^5\text{-}C_5H_5)(L)Cu$ compounds is described and illustrated for compounds with L = $(C_2H_5)_3P$, $(C_4H_9)_3P$, $(C_6H_5)_3P$, $(CH_3O)_3P$, and CH_3NC. The method involves reaction of the appropriate $(LCuI)_4$ or $(LCuBr)_4$ compound with C_5H_5Tl. The compounds have all been characterized by analyses, pmr, infrared and mass spectra, and, for L = $(C_6H_5)_3P$ and $(C_2H_5)_3P$, by X-ray diffraction as *pentahapto*cyclopentadienyl compounds. The compound $(h^5\text{-}C_5H_5)(CO)Cu$ has also been prepared by reaction of CuCl, C_5H_5Tl, and CO in pentane at 0°. It has a very high CO stretching frequency (2093 cm^{-1}) and decomposes rapidly at room temperature.

Recent reports have presented infrared[3] and X-ray evidence[4] to show that $C_5H_5CuPR_3$ compounds have the structure, I, in which there is a *pentahapto*-cyclopentadienyl ring. Our investigations were made feasible by the development of a new general procedure for the preparation of such compounds.



I

Previously, only the compound containing triethylphosphine was known;[5] it was prepared by the reaction of Cu_2O with cyclopentadiene and triethylphosphine. This type of reaction could, perhaps, be applied more generally, but it has practical disadvantages and a more straightforward, general route was sought.

This paper describes such a route, illustrates its application by describing in detail the preparation and characterization of the five compounds $(h^5\text{-}C_5H_5)(L)Cu$, where L = (1) $P(C_2H_5)_3$, (2) $P(C_4H_9)_3$, (3) $P(C_6H_5)_3$, (4) $P(OCH_3)_3$, and (5) $CNCH_3$, and comments briefly on the properties, relative stabilities, and bonding in these compounds. The compound $(h^5\text{-}C_5H_5)(CO)Cu$ has also been prepared by a different method. It is much less stable than the phosphine compounds.

Experimental Section

The preparation and handling of all organometallics was carried out in an atmosphere of prepurified nitrogen, since the h^5-cyclopentadienyl compounds are moderately air sensitive as solids and extremely so when in solution. All solvents were carefully dried in an appropriate manner and were freshly distilled under nitrogen prior to use. Melting points were determined in sealed, nitrogen-filled capillaries.

Considerable difficulty was encountered in obtaining satisfactory elemental analyses, especially for carbon. Best results were obtained from Scandinavian Microanalytical Laboratories, Herlev, Denmark, and Mrs. N. Alvord, of the M.I.T. Microanalytical Laboratory.

Triethylphosphineiodocopper(I),[6] tributylphosphineiodocopper(I),[7] triphenylphosphinebromocopper(I),[8] (trimethyl phosphite)iodo-

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[1] Supported by the National Science Foundation under Grant No. GP 7034X.

[2] National Science Foundation Predoctoral Fellow, 1966–1970.

[3] F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 7281 (1969).

[4] (a) F. A. Cotton and J. Takats, *ibid.*, **92**, 2353 (1970); (b) L. T. J. Delbaere, D. W. McBride, and R. B. Ferguson, *Acta Crystallogr., Sect. B*, **26**, 518 (1970).

[5] (a) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2**, 32 (1956); (b) G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, **89**, 2855 (1967).

[6] G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, 7, 9 (1963).

copper(I),[9] and (methyl isocyanide)iodocopper(I)[10] were prepared by methods in the literature. Mass spectra obtained by the direct injection technique were kindly provided by Dr. R. B. Moyes of Hull University.

(*Pentahapto*cyclopentadienyl)triethylphosphinecopper(I). To 2.0 g (6.5 mmol) of triethylphosphineiodocopper(I) suspended in 100 ml of pentane was added 2.7 g (10 mmol) of thallium cyclopentadienide, and the mixture was stirred for 18 hr at 25°. The reaction mixture was then filtered by suction under nitrogen and the residue was washed with two 20-ml portions of pentane. The total filtrate was reduced to 100 ml by evaporation under vacuum and the solution was then gradually (over a period of 1 hr) cooled to −78°. After the solution had been allowed to remain at −78° for an additional 2 hr, the supernatant liquid was removed from the white crystalline product with a syringe and 25 ml of pentane, precooled to −78°, was used to wash the product. Finally, the product was sublimed for 16 hr at 65° (0.01 Torr) to yield 1.35 g (84%) of white, crystalline product, mp 122–124° (lit.[5] 127–128°).

Anal. Calcd for $C_{11}H_{20}CuP$: C, 53.52; H, 8.18. Found: C, 53.5; H, 8.23.

The pmr spectrum of this compound dissolved in toluene-d_8 had the following resonances (τ values): sharp singlet at 3.85 (5 H) and complex multiplet at 9.0–9.5 (15 H). The h^5-cyclopentadienyl resonance shifts to τ 4.30 in methylcyclohexane solution.

The mass spectrum showed prominent peaks for the parent ion at *m/e* 247 and 249 ($Cu^{63}/Cu^{65} = 2.24$) and intense peaks corresponding to $(C_2H_5)_3PCu^+$ and $(C_2H_5)_3P^+$. As was reported by Whitesides and Fleming,[5b] peaks corresponding to $(C_5H_5)Cu^+$ were quite weak.

(*Pentahapto*cyclopentadienyl)tributylphosphinecopper(I). The procedure just described for the preparation of the triethylphosphine analog was followed using 2.75 g (7 mmol) of tributylphosphineiodocopper(I) and 2.16 g (8 mmol) of thallium cyclopentadienide. Sublimation was accomplished at 70° (0.01 Torr) for 36 hr, to yield 2.25 g (98%) of white, crystalline solid, mp 102–103°.

Anal. Calcd for $C_{17}H_{32}CuP$: C, 61.68; H, 9.76. Found: C, 61.6; H, 9.75.

Pmr spectrum in toluene-d_8: τ 3.83 (sharp singlet, 5 H), 8.6–9.2 (complex multiplet, 27 H). In methylcyclohexane solution the sharp singlet appears at τ 4.12.

The mass spectrum exhibited strong parent ion peaks at *m/e* 331 and 333. Other prominent ions observed corresponded to $(C_4H_9)_3PCu^+$ and $(C_4H_9)_3P^+$.

(*Pentahapto*cyclopentadienyl)triphenylphosphinecopper(I). To 1.70 g (4.2 mmol) of triphenylphosphinebromocopper(I) suspended in 100 ml of THF was added 1.67 g (6.2 mmol) of thallium cyclopentadienide, and the mixture was stirred for 18 hr. Next, the mixture was filtered by suction under nitrogen and the residue washed with 25 ml of THF. The filtrate was evaporated to about 40 ml under high vacuum, 75 ml of hexane was added, and the solution was then cooled to −78°, which caused precipitation of $(h^5\text{-}C_5H_5)CuP(C_6H_5)_3$ as a light tan solid. Supernatant liquid was removed with a syringe and the product was washed with 25 ml of hexane and then dried under high vacuum. This crude material was extracted with 300 ml of ether and the extract was filtered by suction under nitrogen through a small amount of decolorizing carbon. The filtrate was cooled at −78° for 28 hr, and the supernatant liquid was removed from the crystalline product with a syringe. The $(h^5\text{-}C_5H_5)CuP(C_6H_5)_3$ was then washed with two 25-ml portions of ether which had been precooled to −78°, and was dried under high vacuum, yielding 1.0 g (61%) of white or nearly white crystals which exhibited no melting point and began to decompose at about 140°.

Anal. Calcd for $C_{23}H_{20}CuP$: C, 70.66; H, 5.17; P, 7.92. Found: C, 70.6; H, 5.15; P, 7.50.

Pmr spectrum in tetrahydrofuran: τ 2.6 (15 H), 4.09 (5 H). The mass spectrum had parent ion peaks at *m/e* 390 and 392. Strong peaks also occurred for the fragments $(C_5H_5)_3PCu^+$ and $(C_6H_5)_3P^+$.

This compound is less volatile than the alkylphosphine analogs and differs from them also in being virtually insoluble in nonpolar organic liquids.

(*Pentahapto*cyclopentadienyl)(trimethyl phosphite)copper(I). To 1.6 g (5.1 mmol) of (trimethyl phosphite)iodocopper(I) suspended in 100 ml of pentane was added 1.48 g (5.5 mmol) of thallium cyclopentadienide and the mixture was stirred for 16 hr at 25°. The reaction mixture was then filtered by suction under nitrogen and the residue washed with two 20-ml portions of pentane. Evaporation under vacuum was employed to reduce the volume of the filtrate to 75 ml. Next, the solution was slowly cooled to −78° over a period of about 5 hr and was then kept at −78° for 16 hr. The supernatant liquid was removed from the white crystalline product by syringe and the product was washed with two 15-ml portions of −78° pentane and was dried under vacuum. An additional recrystallization was employed to yield 1.00 g (78%) of pale pink, air-sensitive oil, mp *ca.* −10°.

Anal. Calcd for $C_8H_{14}O_3CuP$: C, 38.02; H, 5.59. Found: C, 37.8; H, 5.57.

Pmr spectrum, neat liquid: τ 4.20 (sharp singlet, 5 H), 6.65 (doublet, J = 13.1 Hz, 9 H). The ^{31}P splitting in $[(CH_3O)_3PCuI]_4$ is 12.0 Hz.

(*Pentahapto*cyclopentadienyl)(methyl isocyanide)copper(I). To 1.6 g (6.9 mmol) of finely powdered (methyl isocyanide)iodocopper(I) suspended in 100 ml of pentane was added 1.97 g (7.3 mmol) of thallium cyclopentadienide. After 10 hr of brisk stirring, the reaction mixture was filtered by suction under nitrogen and the filtration residue was extracted with two 20-ml portions of pentane. The combined filtrate was reduced under high vacuum to 100 ml, slowly cooled to −78° over a period of 5 hr, and then allowed to remain at −78° for 16 hr. The supernatant liquid was then removed with a syringe and the crystalline product washed with two 20-ml portions of pentane, precooled to −78°. The crude product was purified by quickly extracting with 50-, 20-, then 20-ml portions of pentane in that order, treatment of the combined extracts with decolorizing carbon, and then rapid suction filtration under nitrogen into a flask precooled to 0°. The filtrate was reduced to 60 ml under vacuum and the product was crystallized as described above. Drying was carried out at −20° under vacuum to yield 0.67 g (57%) of white or pale yellow crystalline product.

This compound is unstable at room temperature and rapidly turns brown, emitting the characteristic odor of methyl isocyanide. Solutions appear to be slightly more thermally stable at room temperature (although they are exceedingly air sensitive), but they slowly deposit metallic copper.

An analysis was performed by rapidly transferring, under nitrogen, a sample into a tared weighing vessel equipped with a ground glass stopper, closing the vessel, weighing it, and then decomposing its contents with nitric acid. Copper was determined iodometrically by standard volumetric procedures.[11]

Anal. Calcd for C_7H_8NCu: Cu, 37.44. Found: Cu, 37.9.

Pmr spectrum in toluene-d_8: τ 3.85 (sharp singlet, 5 H), 8.40 (broadened singlet, 3 H). The low-field singlet shifts to τ 4.32 in methylcyclohexane.

(*Pentahapto*cyclopentadienyl)carbonylcopper(I). To 1.5 g (1.6 mmol) of finely powdered cuprous chloride suspended in 130 ml of pentane was added 4.85 g (1.8 mmol) of thallium cyclopentadienide and 1 drop of $(C_4H_9)_3P$. The reaction vessel was maintained at 0° and with rapid stirring, carbon monoxide was bubbled into the mixture through a fritted glass gas inlet. The reaction was allowed to proceed at 0° for 10 days. During this time, pentane was periodically added to maintain the solution volume at about 130 ml. Toward the end of this period, a copper mirror was visible in some parts of the gas outlet system and the grease in the ground glass joints had turned dark red.

Under an atmosphere of carbon monoxide, the reaction mixture was filtered by suction and the residue washed with two 20-ml portions of pentane. The pale yellow filtrate was maintained at −55° and was distilled under vacuum through a −78° trap. This process was repeated to yield finally about 20 ml of a colorless pentane solution of $(h^5\text{-}C_5H_5)CuCO$ which collected in the −78° trap. During the distillations, a pale yellow, pentane-insoluble residue was observed to form in the distilling vessel and a white film formed in much of the distilling train. A stream of carbon monoxide swept much but not all of these residues into the collection flask, where the solution remained colorless.

The pentane solution of $(h^5\text{-}C_5H_5)CuCO$ began to decompose slowly at room temperature even under an atmosphere of carbon monoxide. Solutions maintained under nitrogen appeared to be considerably less stable. The solutions are air sensitive and deposit a copper-containing green precipitate on oxidation. These pentane solutions also react with phosphines with displacement of carbon monoxide to yield the corresponding $(h^5\text{-}C_5H_5)CuPR_3$ derivatives. In a typical experiment, 5 ml of a freshly distilled

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(10) H. Irving and M. Jonason, *J. Chem. Soc.*, 2095 (1960).

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Table I. Infrared Data for $(h^5\text{-}C_5H_5)(L)Cu$ Molecules

L = $(C_2H_5)_3P$	$(C_4H_9)_3P$	$(C_6H_5)_3P$	$(CH_3O)_3P$	$CNCH_3$	CO	Assignments
3085[a] ms	3085[a] ms	*g*	3095[b] ms	3100[a] ms	*h*	E_1 C–H stretch
				2190 vs[a]		C≡N stretch
					2093 vs[c]	C≡O stretch
998[d] ms, sharp	997[d] ms, sharp	*g*	*f*	1000[d] m, b	*h*	C–H in-plane bending
752[d] vs, vb	755[d] vs, vb	*g*	*Ca.* 775[b,e]	762[d] vs, vb	*h*	C–H out-of-plane wagging

[a] Toluene-d_8 solution. [b] Neat liquid. [c] Pentane solution. [d] Mull. [e] ν_{P-O} interferes. [f] ν_{C-O} interferes. [g] Phenyl group vibrations interfere. [h] Not recorded because of instability of compound.

pentane solution of $(h^5\text{-}C_5H_5)CuCO$, maintained at −78°, was treated with 0.20 ml of $(C_4H_9)_3P$. Agitation of the solution caused gas evolution and the C≡O stretch of $(h^5\text{-}C_5H_5)CuCO$ disappeared from the infrared spectrum. After reduction of the solution volume (under vacuum) to about 2 ml, cooling at −78° caused precipitation of a white crystalline product, which was recrystallized from pentane at −78°, sublimed at 68° (0.05 Torr), and identified as $(h^5\text{-}C_5H_5)Cu[P(C_4H_9)_3]$ by its melting point and pmr spectrum. From the amount of phosphine adduct recovered, it is estimated that the total yield of $(h^5\text{-}C_5H_5)CuCO$ from the reaction was on the order of 100 mg.

The yellow-orange distillation residue, which always appears upon evaporation of $(h^5\text{-}C_5H_5)CuCO$ solutions, invariably regenerates some $(h^5\text{-}C_5H_5)CuCO$ upon treatment with carbon monoxide. Extraction of this material with pentane (in which it is poorly soluble) under an atmosphere of carbon monoxide yields a solution whose ir spectrum is characteristic of $(h^5\text{-}C_5H_5)CuCO$. Extraction with more polar solvents (*e.g.*, toluene or ether) produces orange solutions which are exceedingly air sensitive and whose infrared spectra exhibit, besides the carbonyl stretch of $(h^5\text{-}C_5H_5)CuCO$, other bands in the region of 2000 cm^{-1}. Even under an atmosphere of carbon monoxide, this yellow-orange residue is unstable, turning dark brown within several hours.

The preparation of $(h^5\text{-}C_5H_5)CuCO$ can also be achieved in anhydrous ether solution, using the same procedure as described above. The reaction proceeds much more rapidly than in pentane, but it is even more difficult to achieve any separation of solvent and product.

Spectroscopic Measurements. Proton nuclear magnetic resonance spectra were recorded on Varian Associates A-60 or T-60 spectrometers. The A-60, equipped with a V-6040 temperature controller, was employed for low-temperature studies. Samples were prepared by either of two methods. In one, freeze–thaw-degassed solvent and tetramethylsilane were distilled onto the solid sample and the nmr tube was sealed off under high vacuum. In the other method, the sample was placed in a nitrogen-flushed nmr tube, the tube was capped with a serum stopper, and the degassed solvent was injected by syringe. For thermally unstable compounds, sample solutions were prepared at low temperature and were transferred to cooled, serum-capped sample tubes either by quickly siphoning through stainless steel syringe needle tubing or by means of a syringe, which had been precooled by filling with −78° solvent. Sample solutions prepared by these procedures were stored at −78° until spectra were recorded, at which time the sample tubes were placed in the spectrometer probe, which had already equilibrated at low temperature.

Infrared spectra were obtained with a Perkin-Elmer 337 spectrophotometer and were calibrated with polystyrene film. Routine sample preparation has been described previously.[3] In the case of thermally unstable compounds, solutions were prepared at low temperatures and were kept at −78° until spectra were recorded. At this time, the sample solution was quickly injected into the ir cell by syringe and spectra were recorded immediately. Repeated scans were employed to monitor decomposition. In the case of mull spectra of $(h^5\text{-}C_5H_5)CuCNCH_3$, mulls were prepared and spectra were taken as rapidly as possible. Decomposition was noted by successively recording spectra and observing any changes in various peaks.

Results

All of the compounds except the carbonyl were prepared by a convenient procedure based on the reaction

$$\frac{1}{n}(LCuX)_n + C_5H_5Tl \longrightarrow C_5H_5CuL + TlX$$

where *n* presumably equals 4 and X is a halogen. The yields were generally quite high (57–98%) and the starting materials are readily available and easy to handle. The work-up procedure is simple, generally involving filtration, crystallization, and possibly sublimation. All five compounds are exceedingly air sensitive in solution, but the colorless solids can be handled in air for short periods of time without noticeable discoloration.

The carbonyl compound had to be prepared by a different procedure since no stable $(CuXCO)_n$ compound is known. The reaction used was

$$CuCl + C_5H_5Tl + CO \xrightarrow[0^\circ]{\text{pentane}} C_5H_5CuCO$$

It appears that this reaction is catalyzed to some extent by added phosphines, which apparently form soluble CuCl species. This substance is highly unstable except under an atmosphere of carbon monoxide,[12] and even then it decomposes within an hour at room temperature. As expected, cyclopentadienylcarbonylcopper(I) is quite volatile and hence could not be completely separated from pentane by repeated trap-to-trap vacuum distillation at low temperatures. Distillations invariably leave an air-sensitive yellow residue remaining behind in the distilling vessel, which appears to partially regenerate C_5H_5CuCO upon treatment with carbon monoxide. Treatment of a solution of C_5H_5CuCO at low temperature with tributylphosphine causes immediate displacement of CO and the compound $(h^5\text{-}C_5H_5)[(C_4H_9)_3P]Cu$ can be isolated from the reaction.

The pmr spectra of all six compounds dissolved in saturated hydrocarbon solvents exhibit a sharp singlet at about τ 4.3. The spectrum of C_5H_5CuCO was recorded at −20° to retard decomposition. The position of the cyclopentadienyl resonances in these compounds invariably shifts to lower field in toluene-d_8, sometimes by nearly 0.5 ppm. This displacement to lower field is unusual, since in our experience, aromatic solvents usually shift the proton resonance in $h^5\text{-}C_5H_5$ molecules to higher field, sometimes by as much as 1 ppm. Also, resonance positions as low as τ 3.8 are unusual[13] for $h^5\text{-}C_5H_5$ complexes of metals with formal oxidation numbers of 0 or 1+.

The infrared spectra of these molecules exhibit absorbances characteristic of a *pentahapto*cyclopentadienyl mode of bonding.[3] Infrared data are summarized in Table I. The infrared spectrum of the carbonyl compound has a sharp band at 2093 cm^{-1}, assigned to CO

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(12) This, in general, appears to be a characteristic shared by many unstable metal carbonyl molecules, such as $HCo(CO)_4$: P. Gilmont and A. A. Blanchard, *Inorg. Syn.*, 2, 240 (1946).

(13) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, 3, 1 (1965).

stretching. This band rapidly decays at room temperature as the compound decomposes.

Within the series of $(h^5\text{-}C_5H_5)(L)Cu$ compounds, thermal stability varied greatly, depending upon L. $(h^5\text{-}C_5H_5)[(C_6H_5)_3P]Cu$ appears to be the most stable, decomposition beginning at about 130°. Both $(h^5\text{-}C_5H_5)[(C_2H_5)_3P]Cu$ and $(h^5\text{-}C_5H_5)[(C_4H_9)_3P]Cu$ begin to darken in the region of their melting points (124° and 103°, respectively). After several days at room temperature $(h^5\text{-}C_5H_5)[(CH_3O)_3P]Cu$ samples give slight deposits of metallic copper. The least stable compounds are $(h^5\text{-}C_5H_5)(CH_3NC)Cu$, which darkens after several minutes at room temperature, and $(h^5\text{-}C_5H_5)(CO)Cu$, which decomposes even more rapidly on warming to room temperature. The stabilities of the $(h^5\text{-}C_5H_5)(L)Cu$ compounds thus fall in the order (for L groups)

$$(C_6H_5)_3P > (C_2H_5)_3P \approx (C_4H_9)_3P > (CH_3O)_3P \gg CH_3NC > CO$$

Discussion

As noted previously,[3] molecules of the type $(h^5\text{-}C_5H_5)(L)Cu$ fit naturally into the existing series of isoelectronic $(h^5\text{-}C_5H_5)(L)_nM$ molecules and therefore the presence of the *pentahapto*cyclopentadienyl ring in the copper compounds is not actually surprising, even though it went so long unrecognized. However, the contraction of the 3d orbitals toward the right of the transition series leads to decreased interaction between metal and cyclopentadienyl e_1 and e_2 orbitals and this is reflected in the relatively large distance of the metal atom from the center of the C_5H_5 ring, *viz.*, 1.862 (3) Å,[4] as compared with distances of about 1.75 Å for $(h^5\text{-}C_5H_5)Ni$ groups.[14] Since the 4s and 4p orbitals also decrease in energy toward the right of the transition series, they presumably play an increasingly effective part in metal–ring bonding, ultimately, in $(h^5\text{-}C_5H_5)Tl$ becoming solely responsible for such bonding.[15]

The d orbital contraction must also affect the strength of the metal–L interaction, and it appears that the markedly variable stabilities of the complexes synthesized are manifestations of a lack of available metal π back-bonding orbitals. This is evident in the case of the highly unstable $(h^5\text{-}C_5H_5)(CO)Cu$, where the CO stretching frequency of 2093 cm^{-1} is exceedingly high for a cyclopentadienyl metal carbonyl complex; the frequency in CO itself is 2143 cm^{-1}. The CO bond stretching force constant is calculated to be 17.7 mdyne/Å. Table II compares this value to CO stretching force constants for isoelectronic $(h^5\text{-}C_5H_5)M(CO)_n$ compounds. The force constant for $(h^5\text{-}C_5H_5)V(CO)_4$ is that calculated by Durig, *et al.* (Table II); the others were calculated from the usual CO-factored secular equations.[16] It is quite apparent that back-bonding, *i.e.*, drift of electron density from filled metal 3d orbitals into C≡O π^* orbitals, decreases as $(h^5\text{-}C_5H_5)CuCO$ is approached, and this is in spite of the fact that in the molecules with more than one CO group, there is greater competition for the available π-electron density on the metal. This correlation may, by extension, also explain why copper–carbonyl species in general are unstable and seldom isolated in the solid state.[17,18]

Table II. CO Stretching Force Constants (mdyn/Å) for $(h^5\text{-}C_5H_5)M(CO)_n$ Species[a]

$(h^5\text{-}C_5H_5)M(CO)_n$	k_{CO}	Ref
$(h^5\text{-}C_5H_5)V(CO)_4$	15.6	*b*
$(h^5\text{-}C_5H_5)Mn(CO)_3$	15.6	*c*
$(h^5\text{-}C_5H_5)Co(CO)_2$	16.2	*d*
$(h^5\text{-}C_5H_5)Cu(CO)$	17.7	This work
CO	18.6	

[a] All data are from solution spectra. [b] J. R. Durig, A. L. Marston, R. B. King, and L. W. Hauk, *J. Organometal. Chem.*, **16**, 425 (1969). [c] I. J. Hyams, R. T. Bailey, and E. R. Lippincott, *Spectrochim. Acta, Part A*, **23**, 273 (1967). [d] R. B. King, *Organometal. Syn.*, **1**, 117 (1965).

Infrared data on $(h^5\text{-}C_5H_5)CuCNCH_3$ are informative as to the nature of the copper–isocyanide bond. Generally,[19] coordination to Lewis acids and metals which are poor π donors (*e.g.*, positively charged species) raises the C≡N stretching frequency above that found for the free isocyanide. On the other hand, coordination to metals which are good π donors usually lowers the C≡N frequency. In $(h^5\text{-}C_5H_5)CuCNCH_3$, the $\nu(C{\equiv}N)$ is at 2190 cm^{-1}, which is distinctly higher than that found[19] for free $CNCH_3$, 2158 cm^{-1}. Thus, the interaction between the Cu 3d orbitals and the isocyanide π^* orbitals is weak, though it should be noted that considerably more stable Cu(I) isocyanide complexes with about the same $\Delta\nu(C{\equiv}N)$ have been synthesized.[19] Although isocyanides, unlike CO, are capable of serving as good σ donors, often forming stable bonds to metal atoms in positive formal oxidation states, it must be concluded that dative σ bonding with the copper is not particularly strong in this case.

We are left, then, with some uncertainty as to why the $(h^5\text{-}C_5H_5)(PR_3)Cu$ compounds are much more stable than the carbonyl and isocyanide complexes. It may be that the phosphines allow an optimum combination of σ-donor and π-acceptor functions which cannot be achieved with the other ligands. It is also possible that purely kinetic factors—especially those dependent on the escape of the ligand L because of its volatility—lead to the greater practical stability of the phosphine complexes without their having any greater thermodynamic stability.

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