An Infrared Study of the Structures of Cyclopentadienyl Compounds of Copper(I) and Mercury(II)[1]

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Abstract: The infrared spectra of the copper(I) compounds $(C_5H_5)CuPR_3$, R = C_2H_5, C_4H_9, and the mercury compounds $(C_5H_5)_2Hg$ and C_5H_5HgCl have been reinvestigated. Comparisons are made with the spectra of compounds which serve as models for *pentahapto-* and *monohapto*cyclopentadienylmetal systems. The following conclusions emerge unequivocally: (1) contrary to the belief which has prevailed since 1956, the copper compounds contain *pentahapto* (*i.e.*, "sandwich-bonded") rings, and (2) the mercury compounds contain *monohapto* (*i.e.*, σ-bonded) rings. The significance of these results is discussed in relation to the physical, chemical, and dynamical properties of the molecules.

The first description of a cyclopentadienylcopper compound outside of the patent literature was given by Wilkinson and Piper,[3] who isolated $(C_5H_5)[P(C_2H_5)_3]Cu$ from the reaction of Cu_2O with cyclopentadiene and triethylphosphine. These authors also made the suggestion, with reservations, that this molecule contains a *monohapto*cyclopentadienyl ring. This suggestion has been perpetuated by several subsequent publications.[4,5] However, in the course of a reinvestigation of the pmr spectrum of this compound, and homologous ones with different phosphines, we became doubtful about this structure. Close examination of the evidence for it from vibrational spectra[3] and indeed a review of the entire state of the published correlations[4] between ir spectra and cyclopentadienylmetal configurations indicated to us the need for a thorough, careful reexamination of this problem.

In view of contradictory claims[3,4,6–10] concerning the structures of cyclopentadienyl compounds of mercury(II) the study was extended to include $(C_5H_5)_2Hg$ and $(C_5H_5)HgCl$ as well.

Experimental Section

All organometallic compounds were prepared, stored, and handled in an atmosphere of prepurified nitrogen. Solvents were carefully dried in the manner appropriate to each and then distilled under nitrogen just prior to use. The organomercury compounds were stored at −78°, in the dark.

The $(C_5H_5)(PR_3)Cu$ compounds were prepared by reaction of C_5H_5Tl with the appropriate $[(PR_3)CuI]_4$ compound. The procedures will be described in detail in a forthcoming publication.

Dicyclopentadienylmercury was prepared from TlC_5H_5 and $HgCl_2$ employing the procedure of Nesmeyanov, *et al.*,[11] and was recrystallized several times from ether at low temperature in the dark. Although manipulations involving this substance were performed in normal laboratory light, its exposure to light was otherwise restricted.

Cyclopentadienylchloromercury(II) was prepared from TlC_5H_5 and $HgCl_2$ by the method of Kitching[10] and recrystallized several times from THF–pentane mixtures.

Triethylphosphineiodocopper(I) and tributylphosphineiodocopper(I) were prepared by methods in the literature.[12,13]

Spectroscopic Measurements. Solutions of the mercurials were prepared in subdued light immediately before spectroscopic examination. Samples were monitored for decomposition by observing changes in the relative intensities of various peaks during the course of several scans. A nitrogen-filled glove bag was employed for the preparation of solutions and mulls of the copper compounds and for filling cells; samples were again monitored for decomposition. All solvents and mull media were examined by infrared spectroscopy to identify spurious peaks which might be present.

Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrometer, and frequency calibration was done with polystyrene film. The C–H stretching regions were also studied at higher resolution with a Perkin-Elmer 521 grating spectrometer which had previously been calibrated.

Results

Reference Compounds. The chief reference compound for the *pentahapto*cyclopentadienylmetal group is $(h^5\text{-}C_5H_5)NiNO$, the spectrum[14] of which is shown in the center of Figure 1. However, due consideration was also given to several other compounds, namely $(h^5\text{-}C_5H_5)Mn(CO)_3$,[15] $(h^5\text{-}C_5H_5)V(CO)_4$,[16] and ferrocene.[17] A simple symmetry analysis in terms of internal coordinates for the C_5H_5 part of an $M\text{–}C_5H_5$ system with C_{5v} symmetry shows that there should be 14 normal modes of vibration, of which 7 will be infrared active. On the basis of the experimental observations and previously proposed assignments for the reference compounds just mentioned, the descriptions, intensities, and approximate frequencies of the infrared-active fundamentals localized in the C_5H_5 ring of an $(h^5\text{-}C_5H_5)M$ group are summarized in Table I.

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

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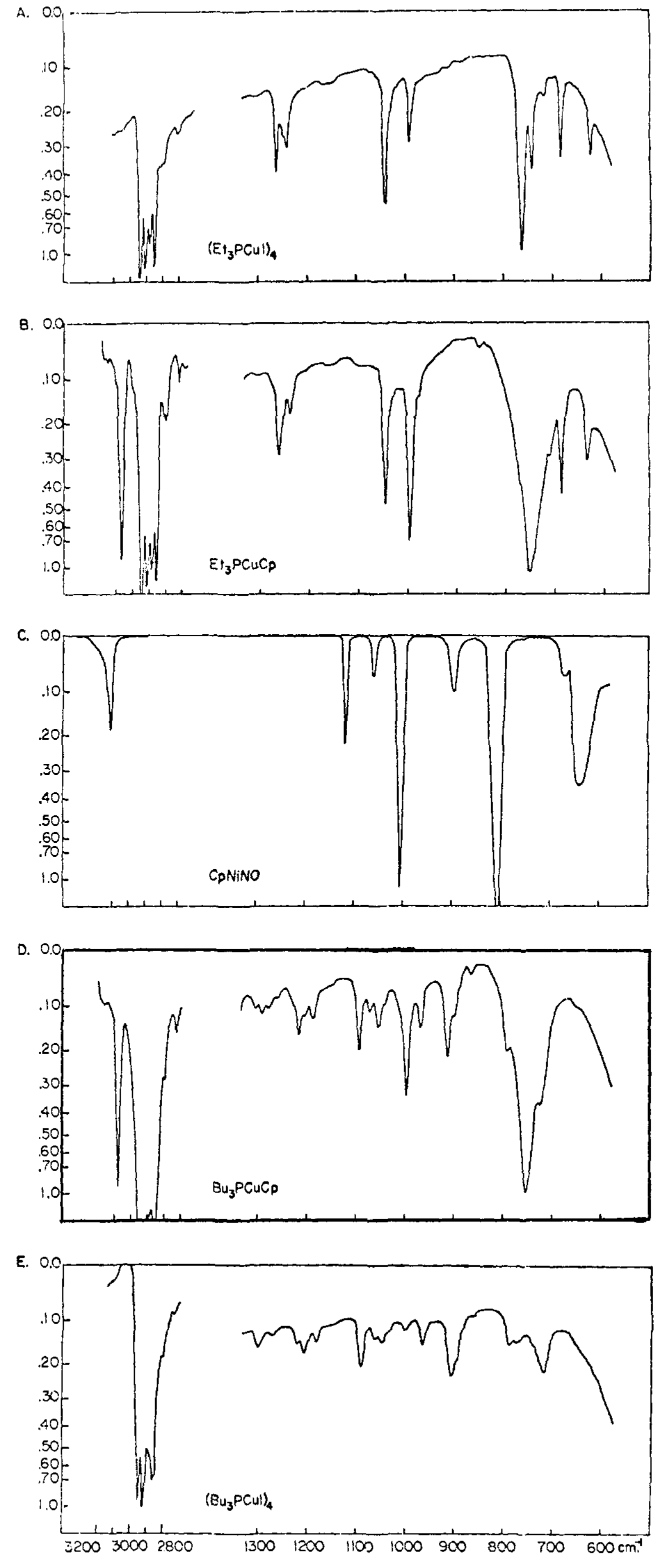
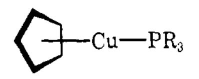


Figure 1. A. The infrared spectrum of $[(C_2H_5)_3PCuI]_4$. The high-frequency region was recorded as a Fluorolube mull and the low-frequency region as a Nujol mull. B. The infrared spectrum of $(h^5\text{-}C_5H_5)CuP(C_2H_5)_3$. The high-frequency region was studied in toluene-d_8 solution (the Fluorolube mull spectrum was essentially identical, but with a poorer signal to noise ratio) and the lower region as a Nujol mull. C. The infrared spectrum of $(h^5\text{-}C_5H_5)NiNO$, redrawn from ref 14. D. The infrared spectrum of $(h^5\text{-}C_5H_5)CuP(C_4H_9)_3$. The high-frequency region was studied as a solution in toluene-d_8 (the Fluorolube mull spectrum was essentially identical, but weaker) and the low-frequency region as a Nujol mull. E. The infrared spectrum of $[(C_4H_9)_3PCuI]_4$. The high-frequency region was recorded as a Fluorolube mull and the lower region as a Nujol mull.

From Table I it is clear that the infrared spectrum expected for an $(h^5\text{-}C_5H_5)M$ system in the range of ~600 to ~3500 cm^{-1} is very simple indeed, consisting of a medium band at 3050–3100 cm^{-1}, a strong band at ~1000 cm^{-1}, and a broad, very strong band at 800 ± 50 cm^{-1} with the possibility of two more bands, perhaps very weak, at ~1400 cm^{-1} and ~1100 cm^{-1}. No further bands of appreciable intensity are to be expected, since the foregoing list accounts for all fundamentals. The spectrum of $(h^5\text{-}C_5H_5)NiNO$ seen in Figure 1 accords well with this summary.



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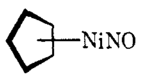

II

For an $(h^1\text{-}C_5H_5)M$ system, which can have at best C_s symmetry, there are 24 normal modes of vibration arising in the C_5H_5 group itself and presumably all of them will have frequencies above 600 cm^{-1}. The only possible exceptions might be one or two of the four ring deformation modes. Five of the total of 24 modes are C–H stretches. One, the MC–H stretch, may be expected in the region of aliphatic C–H stretches, *viz.*, 2800–3000 cm^{-1}, while the other four, the olefinic C–H stretches, should come between 3000 and 3100 cm^{-1}. It would be entirely reasonable that of four such closely spaced bands only three might be resolved clearly. There should then be 18–20 fundamentals spread through the region from $\leq$1600 (C=C stretching) to $\geq$600 cm^{-1}. Thus a *very* rich and complex spectrum is to be expected in marked contrast to theory and observation for $(h^5\text{-}C_5H_5)M$ systems.

As a reference standard for the *monohapto*cyclopentadienylmetal system we have used $(CH_3)_3GeC_5H_5$. It has been definitively shown by Davison and Rakita[18] that this is a fluxional molecule containing a *monohapto*-cyclopentadienyl ring. The rate of rearrangement at room temperature is of the order of 10^2–10^3 sec^{-1}, that is, slow enough so that there can be no question of this rearrangement process significantly perturbing the vibrational spectrum. Figure 2 shows the spectrum of $(CH_3)_3GeC_5H_5$. By comparison with numerous spectra of $(CH_3)_3Ge$ derivatives reported in the literature[19] and with the spectrum of $(CH_3)_3GeC{\equiv}CGe(CH_3)_3$ made available to us by Professor D. Seyferth and Mr. D. L. White, it is relatively easy to identify those bands which are due, at least in part, to vibrations essentially resident in the $(CH_3)_3Ge$ portion of the molecule. Such bands are indicated with crosses on the spectrum of $(CH_3)_3GeC_5H_5$ in Figure 2. It is clear that even when these bands are eliminated, the remaining spectrum is very rich and complex as expected.

Cyclopentadienylcopper Compounds. Immediately above and below the reference spectrum ($(h^5\text{-}C_5H_5)NiNO$) in Figure 1 are the spectra of the $C_5H_5CuPR_3$ compounds, and each of these is flanked by the spectrum of the corresponding $[R_3PCuI]_4$ compound. The spectra below 1400 cm^{-1} were recorded on mulls of the solid compounds because the $C_5H_5CuPR_3$ compounds are reactive toward CS_2 and halocarbons which would normally be used to get a complete record of the spectrum in the desired regions. In the C–H stretching

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(18) A. Davison and P. E. Rakita, submitted for publication.

(19) R. J. Cross and F. Glockling, *J. Organometal. Chem.*, 3, 146 (1965), and references therein.

Table I. Infrared-Active Fundamental Vibrational Transitions for the C_5H_5 Ring in an (h^5-C_5H_5)M System

Type of internal coordinate change[a]	Symmetry type	Approx frequency, cm^{-1}	Comments
C–H stretching	a_1	3050–3100	a_1 mode usually vw; only e_1 mode consistently seen
	e_1		
C–C stretching	a_1	~1100	Sym ring breathing; intensity highly variable; often vw
	e_1	~1400	usually m to w
C–H out-of-plane wagging	a_1	~800	Usually broad absorption; combined intensity very high; position varies greatly
	e_1		
C–H in plane wagging	a_1	~1000	Generally strong and close to 1000 cm^{-1}

[a] We follow here the original assignments of Lippincott and Nelson[17]; revisions have since been proposed.[4] Our structure conclusions are not altered by such changes, however.

region, however, solutions in perdeuteriotoluene were used.

The spectra of the $[R_3PCuI]_4$ compounds should be virtually identical with those parts of the $C_5H_5CuPR_3$ spectra which arise from the $CuPR_3$ portions of the molecules. Moreover, it seems safe to assume that there will be no more than slight interactions between the vibrations in the C_5H_5 portions of the molecules. Thus, by inspection, one may delete from the observed spectra of the $C_5H_5CuPR_3$ compounds the "PR_3 bands" so as to leave, barring some possible uncertainties caused by overlap, the spectra of the C_5H_5 rings in these molecules.

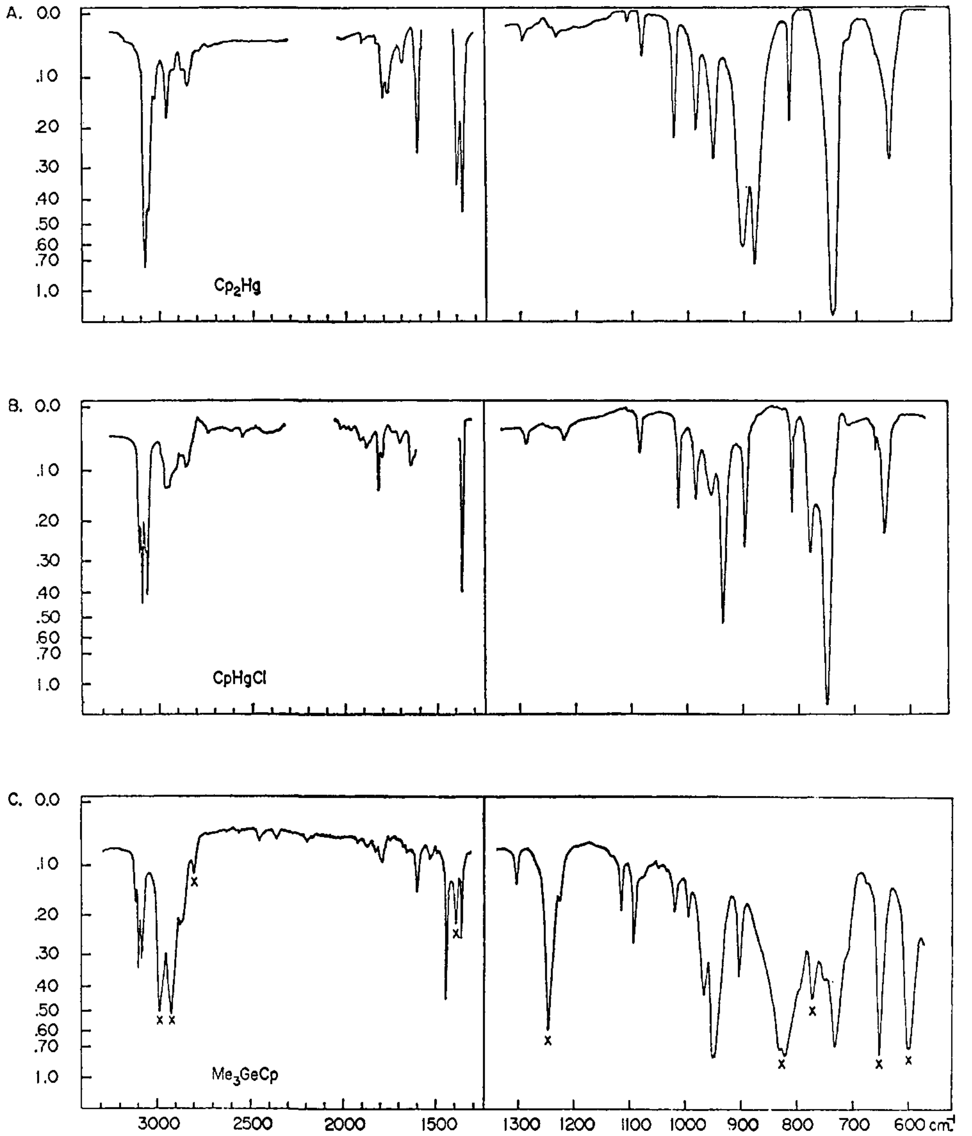

Figure 2. A. The infrared spectrum of (h^1-C_5H_5)$_2$Hg in carbon disulfide. B. The infrared spectrum of (h^1-C_5H_5)HgCl in carbon disulfide. C. The infrared spectrum of (h^1-C_5H_5)Ge(CH_3)$_3$ as a film of the pure liquid. This spectrum was supplied by Professor A. Davison and Mr. P. E. Rakita. Bands marked X are believed to be due to the Ge(CH_3)$_3$ part of the molecule.

Table II lists the bands so identified. Overlap of PR_3 and C_5H_5 absorptions around 1400 cm^{-1} does, in fact, make it impossible to ascertain whether there is actually a medium or weak C_5H_5 band in this region, but otherwise the results are straightforward. It is abundantly clear that the $C_5H_5CuPR_3$ compounds possess extremely simple "C_5H_5 spectra" in the 600–1350 cm^{-1} region. The spectra are far too simple to be consistent with the presence of *monohapto*cyclopentadienyl rings, but correlate satisfactorily with our expectations for a *pentahapto* ring as summarized in Table I.

Table II. Infrared Bands Assignable to C_5H_5 Groups in the $C_5H_5CuPR_3$ Compounds[a]

$C_5H_5CuP(C_2H_5)_3$	$C_5H_5CuP(C_4H_9)_3$	Remarks
3085 m, sharp	3085 m, sharp	Spectrum measured in toluene-d_8
998 ms, sharp	997 ms, sharp	Mull spectrum
752 vs, vb	755 vs, vb	Mull spectrum

[a] m = medium; v = very; s = strong; b = broad.

The spectra in the C–H stretching region supply additional strong evidence that *pentahapto* rings are present. Only a single sharp peak is seen between 3000 and 3100 cm^{-1}. This is attributable to the e_1 mode, the a_1 mode being, as usual,[20] too weak to be seen. This result is in marked contrast to the multiple olefinic C–H stretching bands expected for a *monohapto*cyclopentadienylmetal system and clearly observed in $(CH_3)_3GeC_5H_5$ (see Figure 2).

Cyclopentadienylmercury Compounds. The spectra of $(C_5H_5)_2Hg$ and C_5H_5HgCl, measured on CS_2 solutions, are shown in Figure 2. The spectrum of $(C_5H_5)_2Hg$ in CCl_4 was also recorded and it is essentially identical with that in CS_2. Two things are immediately clear; first, the spectra of the two mercurials are very similar to each other. Second, they are both very similar to what remains of the spectrum of $(CH_3)_3GeC_5H_5$ after bands due to the CH_3 groups have been deleted. In the region from 600 to 1350 cm^{-1} the general similarities of these three relatively complex spectra leave no doubt that the mercurials contain *monohapto*cyclopentadienyl groups.

The C–H stretching region again affords strong evidence for the type of cyclopentadienyl–metal configuration present. Both $(C_5H_5)_2Hg$ and C_5H_5HgCl show multiple absorptions in the olefinic C–H stretching region, although the resolution is noticeably poorer in the case of $(C_5H_5)_2Hg$. Nevertheless, there is no doubt that the absorption here is multiple, closely akin to that in $(C_5H_5)HgCl$ and $(CH_3)_3GeC_5H_5$ and quite different from the single, sharp, peak at ~3085 cm^{-1} which is characteristic of (h^5-C_5H_5)M systems. For a (h^1-C_5H_5) ring there should also be an aliphatic C–H stretching band; presumably the bands occurring at 2960 cm^{-1} in $(C_5H_5)_2Hg$ and C_5H_5HgCl can be so assigned, although assignments in the 2800–2000 cm^{-1} region are somewhat ambiguous because the model compounds absorb here and because there is also a weak band at ~2850 cm^{-1}. The latter is, however, most likely an overtone or combination band and it may owe some of its intensity to Fermi resonance with the aliphatic C–H stretch.

Table III. Infrared Spectra (cm^{-1}) of *Monohapto*cyclopentadienylmetal Groups

$(C_5H_5)_2Hg$[a]	C_5H_5HgCl[a]	$C_5H_5Ge(CH_3)_3$[b]	$(CH_3)_3GeC\equiv CGe(CH_3)_3$[c]
3095 ms	3110 m	3110 m	
3088 ms	3095 m	3090 m	
3067 ms	3077 m	3070 m	
3040 w, sh	3070 m		
		2975 vs	2980 vs
		2910 vs	2915 vs
2960 m	2960 m		
2850 w	2855 w	2860 m	
		2800 w	2800 w
	1880 vw		
1800 m	1820 w	1838 vw	
1780 m	1805 w	1800 w	
1695 w	1700 vw		
1610 m	1645 w	1617 m	
1530 w	1543 w	1540 w	
1427 m	1461 m	1458 s	
1400 m		1402 m	1410 m
1370 s	1370 m	1378 m	
1282 w	1290 w	1295 m	
		1238 vs	1240 vs
1231 w	1222 w	1220 w	
1108 w		1110 m	
1082 m	1086 w	1087 m	
1023 m	1015 m	1015 w	
987 m	985 m	995 w	
995 m	958 w	960 m	
904 s	936 s	944 vs	
883 s	897 m	900 m	
		860 w	
		826 vs	
		826 vs	826 vs
820 m	812 m	817 vs	
		795 w	
	780 w	770 w	
		748 w	765 m
742 vs	750 vs	729 vs	
712 w	712 vw	710 vw	
665 vw	665 vw	672 vw	
641 m	649 m	650 vs	668 vs
		597 vs	608 s

[a] Measured in CS_2 solution. [b] Measured as a neat liquid film. [c] Combined data from CCl_4 solution and mineral oil mull.

The observed spectra for the h^1-C_5H_5 compounds are summarized in Table III.

Discussion

Cyclopentadienylcopper(I) Compounds. The important conclusion, which emerges very clearly, is that these compounds contain *pentahapto* and not *monohapto* rings. It is certainly rather curious that the incorrect formulation has remained unchallenged for some 13 years. It should be noted that the original suggestion[3] of a *monohapto* ring was not supported by any strong experimental evidence and was put forth only in a qualified way. It would seem, however, that even at that time the infrared data might have appeared more in support of a *pentahapto* ring, though material for comparison was considerably less abundant then. The subsequent assignment[4] of a *monohapto* structure on the basis of infrared data is more difficult to justify. In both of the earlier publications little attention was paid to the C–H stretching region (it was not even reported in one case[4]). This may have been due to the fact that the poor resolution (~20 cm^{-1}) ob-

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(20) The expectation that this vibration will absorb only weakly has previously been discussed in detail, *cf.* F. A. Cotton and L. T. Reynolds, *J. Amer. Chem. Soc.*, **80**, 269 (1958).

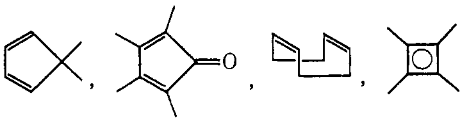
tainable in this region with a rock salt prism obscures significant structure. From the present study it is evident that this region of the spectrum, observed under adequate resolution, can be singularly informative.

It is worth commenting on the fact that the *pentahapto* structure, I, for $(C_5H_5)CuPR_3$ compounds need not be considered at all surprising. Such molecules are isoelectronic with $(h^5\text{-}C_5H_5)NiNO$ which has structure[21] II. The idea that d orbitals suitable for bonding interactions with the C_5H_5 ring will be markedly less available in $C_5H_5CuPR_3$ than in C_5H_5NiNO is certainly not plausible. Indeed, it is possible to view the $(h^5\text{-}C_5H_5)$-$CuPR_3$ molecules as members of a rather long isoelectronic sequence in which we have $(h^5\text{-}C_5H_5)M$ moieties interacting with 5-, 4-, 3-, 2-, and, hypothetically as yet, 1-electron ligands, *viz.*

$(h^5\text{-}C_5H_5)Fe(h^5\text{-}C_5H_5)$ (ferrocene)

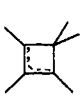
$(h^5\text{-}C_5H_5)CoL$

L =



, 2CO

$(h^5\text{-}C_5H_5)NiNO$, $(h^5\text{-}C_5H_5)NiL$, L =



$(h^5\text{-}C_5H_5)Cu\ PR_3$

$[(h^5\text{-}C_5H_5)Zn\text{-}R,\ R = \text{alkyl?}]$

$[(h^5\text{-}C_5H_5)M,\ M = \text{In, Tl, Ga?}]$

From this point of view the *pentahapto* structure might be considered as that which is logically expected, rather than in any sense surprising. The question of whether the series does in fact extend to the zinc and gallium compounds is of some interest, and is under investigation.

It should be recognized, however, that the amount of d orbital participation in $(h^5\text{-}C_5H_5)$–M bonding must decrease continuously in the above series, while the role of the e_1-type p orbitals (p_x and p_y when the 5-fold axis is called the *z* axis) will steadily increase as the p orbitals drop in energy and become less diffuse. In the case of $(h^5\text{-}C_5H_5)Tl$, the 6p orbitals of thallium are evidently very well suited for overlap with the ring e_1 orbitals.[22] In $(h^5\text{-}C_5H_5)In$, which is much less stable than the thallium compound, the p-orbital overlap may be less effective. In any case, the inherent stability of the I oxidation state is lower for In than for Tl. The expected continuation of both trends as we go from In to Ga makes it problematical whether $(h^5\text{-}C_5H_5)Ga$ is capable of existence at ordinary temperatures, but experimental study seems worthwhile.

Another fact worthy of note in connection with the reasonableness of structure I is the remarkable chemical and thermal stability of the cyclopentadienylcopper(I) compounds; $C_5H_5CuP(C_2H_5)_3$ can be sublimed under vacuum at 70°, while other organocopper compounds decompose thermally well below 0°[23] and are rapidly hydrolyzed by water. Clearly, the enormously greater stability of the cyclopentadienyl compounds would be difficult to explain if conventional *monohapto*cyclopentadienylcopper structures were correct.

It is in fact an interesting historical irony that a precisely parallel situation prevailed with dicyclopentadienyliron. Immediately following Kealy and Pauson's report[24] of the isolation of $(C_5H_5)_2Fe$ and their discussion of it as a bis-$(h^1\text{-}C_5H_5)_2Fe$ molecule despite the fact that its "remarkable stability" was "of course, in sharp contrast to the failures of earlier workers to prepare similar compounds" with other R groups, Wilkinson, Rosenblum, Whiting, and Woodward[25] rejected the *monohapto*-cyclopentadienyl structure at least partly on the ground that the exceptional stability of ferrocene in comparison to other (nonexistent) organoiron species "led us to consider whether an alternative to the structure might be more nearly in accord with the unique character of Kealy and Pauson's compound." The close similarity to the situation with $C_5H_5CuPR_3$ compounds has previously been overlooked.

Cyclopentadienylmercury(II) Compounds. The spectra demonstrate unequivocally that these molecules do not contain *pentahapto* rings, as has been claimed by some workers.[7] Moreover, the spectra seem to us to be quite consistent with the presence of a *monohapto* ring in C_5H_5HgCl and with the presence of two such rings in $(C_5H_5)_2Hg$. The complexity of the $(C_5H_5)_2Hg$ spectrum requires the presence of at least one $(h^1\text{-}C_5H_5)$ ring. The possibility that the latter compound might contain one $(h^5\text{-}C_5H_5)$ and one $(h^1\text{-}C_5H_5)$ ring seems very remote indeed, since the differences between the $(C_5H_5)_2Hg$ and C_5H_5HgCl spectra are minor and not consistent with the expected result of adding to the C_5H_5HgCl spectrum the bands arising from a $(h^5\text{-}C_5H_5)M$ group.

Shortly after the completion of our work, Maslowsky and Nakamoto[26] reported a study of the infrared spectra of $(C_5H_5)_2Hg$, C_5H_5HgCl, C_5H_5HgBr, and C_5H_5HgI. They have reached the same conclusions as we did, namely, that only $(h^1\text{-}C_5H_5)$ rings are present in these molecules. Their experimental data are in excellent agreement with ours. We have given the present brief account of our study of $(C_5H_5)_2Hg$ and C_5H_5HgCl since our approach, in terms of choice of reference compound ($C_5H_5Ge(CH_3)_3$, which we think is more appropriate in certain respects than C_5H_6), and emphasis on the C–H stretching region, not only substantiates but supplements theirs.[27]

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[27] NOTE ADDED IN PROOF. (a) A complete X-ray diffraction study of $C_5H_5CuP(C_6H_5)_3$ by F. A. Cotton and J. Takats has confirmed the *pentahapto* bonding. The C_5H_5Cu group has virtually perfect C_{5v} symmetry. (b) A detailed account of the methods of preparing $C_5H_5CuPR_3$ and other C_5H_5CuL compounds is in preparation. (c) The presence of an $h\text{-}C_5H_5$ ring in C_5H_5HgCl has recently been demonstrated by nmr data by P. West, M. C. Woodville, and M. D. Rausch, *J. Amer. Chem. Soc.*, **91**, 5649 (1969).