the reorganization energy—change in E(total)—and the acceptor orbital energy—E(LUMO)—for BF_3 and BCl_3 with varying degrees of angular distortion. A striking feature of these results is that the BCl_3 curves are similar to those of BF_3 but shifted to lower energy. When d orbitals are included in the calculation for BCl_3 the total rise in E(total) and drop in E(LUMO) are about one-third of those given in Figure 5 and the curves are shifted to lower energy. While the CNDO/2 calculations are ambiguous concerning reorganization energies, they do indicate that BCl_3 should be a stronger electron acceptor than BF_3 for any degree of reorganization.

In summary, B–N bond length and force constant data indicate that relative B–N bond strengths are of the same order as relative heats of complex formation for $F_3B\cdot NCCN_3$ and $Cl_3B\cdot NCCH_3$. This result is contrary to previous estimates of reorganization energies which indicate that B–N bond strengths are not a determining factor in complex stability and which lead one to the conclusion that donor–acceptor bond energies are actually the reverse of stabilities.[4] We must look to other effects to explain all of the available information on B–N bond lengths, force constants, and heats of complex formation. One alternate explanation of the data, which appears to merit serious consideration, is the interplay between BX_3 reorganization and acceptor strength, such that the most easily reorganized acid (presumably BCl_3) will be distorted to a greater extent and therefore have a greater electron affinity than its less pliable counterpart.[5] Another possible origin of the increased B–N bond strength for the BCl_3 adduct may be the greater electron affinity for BCl_3 than BF_3 due to less p_π–p_π bonding between Cl and B.[28] While the acidity difference between these boron halides is chemically important, it is small enough that a definitive illustration of its origins is beyond the capabilities of current theory, but there is an indication from CNDO calculations that the greater electron affinity of BCl_3 may be a significant factor. It is therefore probable that both factors mentioned above operate in unison to yield a higher acidity for BCl_3 than for BF_3.

Acknowledgment.—We are grateful to the NSF for the support of this work through Grant GP 6676 and to the Advanced Research Projects Agency for support through the Northwestern Materials Research Center. We thank Professor R. C. Taylor for a copy of P. D. H. Clippard's thesis and for helpful correspondence.

[28] While it probably is not decisive, one contribution to the stability trend is an increase in lattice energy for the heavier complexes. The present observation of increasing intermolecular coupling with increasing halide atomic number affords experimental evidence for the expected trend in intermolecular interactions arising from London and polar forces.

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Trends in $(CH_3)_2YAuP(C_6H_5)_3$ Compounds ($Y^- = Cl^-, CH_3^-, \sigma\text{-}C_5H_5^-$). Proton Magnetic Resonance and Vibrational Spectra[1]

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The new compounds R_2AuXPR_3 obtained by bridge cleavage of dimethylgold(III) halides can be alkylated cleanly. This method has been used to prepare the known compounds $(CH_3)_3AuP(C_6H_5)_3$ and $(CH_3)_3AuP(C_2H_5)_3$ and the new compound $(\sigma\text{-}C_5H_5)(CH_3)_2AuP(C_6H_5)_3$. Complete laser Raman, infrared, and pmr spectra are given for these compounds as well as for $(CH_3)_2AuClP(C_6H_5)_3$ permitting comparisons in the sequence of compounds $(CH_3)_2YAuP(C_6H_5)_3$ ($Y^- = Cl^-, CH_3^-, \sigma\text{-}C_5H_5^-$). Raman spectra establish that the cyclopentadienyl group in $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ is σ bonded, and the pmr spectra establish that it is trans to a methyl group and stereochemically nonrigid as would be expected by analogy with bis(cyclopentadienyl)mercury. Unlike the related $(\sigma\text{-}C_5H_5)(CH_3)_2Tl$, there is no intermolecular exchange of the cyclopentadienyl ligands at 40°. Replacement of Cl^- by CH_3^- leads to a weakening of the Au–C bonds as indicated by a decrease in the frequency of the very intense Au–C stretching bands. Substitution of $\sigma\text{-}C_5H_5^-$ for CH_3^- causes a maximum shift of only 4 cm^{-1} in these frequencies. The trialkyl derivatives show a large trans influence for the alkyl groups leading to a weakening of the mutually trans Au–C bonds.

Introduction

While dialkylgold(III) compounds are among the most stable of the σ-bonded transition metal alkyls, the trialkyl derivatives are considerably less so. Gilman and Woods[4] were able to isolate trimethylgold as the adducts with ethylenediamine, 2-aminopyridine, and benzylamine. These compounds were moderately stable, particularly the ethylenediamine complex, but even it was very light sensitive and detonated upon heating.

Coates and Parkin[5] isolated stable adducts of trimethylgold with trimethyl- and triphenylphosphine either by displacing ethylenediamine from $[(CH_3)_3Au]_2en$ with the phosphine in solution at $-20°$ or by adding the phosphine directly to an ether solution of trimethylgold at $-65°$. A review of organogold chemistry has appeared recently.[6]

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[2] NSF undergraduate participant under Grant GY-5845.

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Studies on the stereochemistry and bonding of complexes with triphenylphosphine ligands are difficult, since the intense $P(C_6H_5)_3$ absorptions dominate the infrared spectra and obscure the skeletal vibrations. No Raman or nmr spectra have been reported previously for the trimethylgold(III) compounds.

In order to study trends in the structure and bonding of compounds of the type $(CH_3)_2YAuP(C_6H_5)_3$, we have synthesized $(CH_3)_3AuP(C_6H_5)_3$ by alkylation of $(CH_3)_2AuIP(C_6H_5)_3$. This has been extended to the preparation of the new compound $(\sigma\text{-}C_5H_5)(CH_3)_2AuP(C_6H_5)_3$. Spectra of the new compound $(CH_3)_2AuClP(C_6H_5)_3$ have been recorded for comparison.

Experimental Section

General Data.—The starting material for the synthesis of the gold compounds was $[(CH_3)_2AuI]_2$, prepared as described by Brain and Gibson.[7] All compounds were handled under a nitrogen atmosphere. Microanalyses were performed by the microanalytical laboratory of this department. Melting points were determined with a Thomas-Hoover capillary melting point apparatus.

Chlorodimethyl(triphenylphosphine)gold.—A solution of $[(CH_3)_2AuCl]_2$[8] (0.097 g, 0.00037 monomol) in 1 ml of cyclopentane was added to a solution of the stoichiometric amount of $P(C_6H_5)_3$ dissolved in 3 ml of cyclopentane. The crystalline compound which appeared immediately was collected on a frit, washed with cyclopentane, and dried under vacuum over P_4O_{10} at *ca.* 5°; mp 155–158° dec. *Anal.* Calcd for $C_{20}H_{21}ClPAu$: C, 45.7; H, 4.00; Cl, 6.76; P, 5.91; Au, 37.5. Found: C, 45.8; H, 4.10; Cl, 7.15; P, 5.87; Au, 37.6.

Trimethyl(triphenylphosphine)gold.—To a solution of $[(CH_3)_2AuI]_2$ (0.0065 monomol) in 25 ml of anhydrous cyclopentane was added a solution of triphenylphosphine (0.0069 mol) in a cyclopentane–anhydrous ether mixture (8:1 v/v). The white precipitate of $(CH_3)_2AuIP(C_6H_5)_3$ which resulted was washed several times with cyclopentane at 0° and dried under vacuum. To a solution of $(CH_3)_2AuIP(C_6H_5)_3$ (0.0036 mol) in anhydrous ether was added an ether solution of CH_3Li (0.0072 mol) at −10°. The solution was stirred for 3 hr during which time the temperature was allowed to rise to 15°. The solution was recooled to 0°, H_2O (10 ml) was added, and the organic layer was separated and evaporated under nitrogen to yield colorless crystals of $(CH_3)_3AuP(C_6H_5)_3$. The product was recrystallized from hexane, mp 118–119°, lit.[5] mp 120° dec. *Anal.* Calcd for $C_{21}H_{24}PAu$: C, 50.0; H, 4.80; P, 6.14; Au, 39.0. Found: C, 50.0; H, 4.59; P, 5.92; Au, 38.9.

Trimethyl(triethylphosphine)gold.—To a solution of $[(CH_3)_2AuI]_2$ (0.0060 monomol) in 50 ml of cyclopentane was added dropwise excess $P(C_2H_5)_3$. The solvent and excess $P(C_2H_5)_3$ were evaporated first in a stream of nitrogen and finally under vacuum. The resulting liquid was dissolved in 100 ml of ether and cooled to 0°, and a solution of CH_3Li (*ca.* 0.016 mol) in ether was added. The mixture was stirred for 2 hr under a nitrogen atmosphere during which time it was allowed to warm to 16°. After recooling to 0°, 10 ml of ice water was added, the two phases were separated, the aqueous phase was discarded, and the ether solvent was evaporated first in a stream of nitrogen and then under vacuum (5 μ) yielding a colorless liquid. *Anal.* Calcd for $C_9H_{24}PAu$: C, 30.0; H, 6.72; P, 8.60; Au, 54.7. Found: C, 30.1; H, 6.59; P, 8.41; Au, 54.4.

σ-Cyclopentadienyldimethyl(triphenylphosphine)gold.—To a solution of $(CH_3)_2AuIP(C_6H_5)_3$ (0.0057 mol) in 25 ml of tetrahydrofuran was added cyclopentadienyl sodium (8 ml, 18%, 0.015 mol) dropwise at −10°. The solution was allowed to warm to 15°, was stirred for 1 hr, and was recooled to 0°; H_2O (10 ml) was added, and the mixture was extracted with petroleum ether (bp 60–68°), which was then evaporated under nitrogen. The product was washed repeatedly with small quantities of ether. Recrystallization from ether yielded pale yellow crystals, mp 99° dec. *Anal.* Calcd for $C_{25}H_{26}PAu$: C, 54.2; H, 4.73; P, 5.59; Au, 35.5. Found: C, 54.2; H, 4.74; P, 5.89; Au, 35.8.

Raman Spectra.—These were obtained using He–Ne excitation and two spectrophotometers. The first is built around a Spex Model 1400 monochromator and has been described briefly elsewhere.[9] The second was a Jarrell Ash 125-300 system with a Spectra Physics 125 He–Ne laser. The compounds were run as solutions, neat liquids, or crystalline powders in sealed capillary tubes using the transillumination technique. Approximately 25 mg of solid or 25 μl of solution samples was employed. Depolarizations were determined with the Spex instrument using a $\lambda/2$ plate in the laser beam and a polarization scrambler before the slit. For these measurements, no analyzer was used (ρ depolarized band = $^6/_7$). Signals were integrated using a Gelman planimeter. Calibration of the monochromators was effected with the exciting line (6328 Å), background plasma lines, and neat indene. Frequencies are corrected to vacuum at 15° and for sharp lines are accurate to ± 2 cm^{-1}.

Infrared Spectra.—These were recorded with a Beckman IR-12 spectrometer using split mulls, solutions, or neat liquids. The instrument was calibrated with polystyrene film and indene. The frequencies for sharp bands are accurate to ± 2 cm^{-1}, while those for broad bands should be within ± 5 cm^{-1}.

Proton Magnetic Resonance Spectra.—A Varian A-60 spectrometer was used for pmr spectra. The ambient probe temperature was *ca.* 40°. Coupling constants are accurate to ± 0.5 Hz; chemical shifts, to 0.01 ppm. TMS was used as an internal reference, and the Gelman planimeter was also used for signal integration.

Data and Results

Proton Resonance Spectra.—The chemical shifts and $^3J(^{31}P\text{–}H)$ coupling constants for the methyl protons bound to gold in $(CH_3)_2AuClP(C_6H_5)_3$, $(CH_3)_3AuP(C_6H_5)_3$, $(CH_3)_3AuP(C_2H_5)_3$, and $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ are collected in Table I. Any coupling between the nonequivalent protons in these compounds was too small to be detected. The cyclopentadienyl protons of $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ gave one resonance split by coupling with ^{31}P, τ 4.43 ppm, and $J(^{31}P\text{–}H) = 2.8$ Hz. The relative intensity of the two high-field doublets to the low-field doublet was 1.25 ± 0.07 (theoretical 1.20). The two main bands in the $P(C_6H_5)_3$ resonance (CCl_4 solution) were shifted 0.08 ppm to lower field relative to the free ligand in $(CH_3)_3AuP(C_6H_5)_3$, and only one intense peak was observed with $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ 0.15 ppm to lower field than the center of the free $P(C_6H_5)_3$ resonances. There was no evidence for any dissociation of triphenylphosphine in any of these complexes.

TABLE I

PROTON MAGNETIC RESONANCE DATA

Compound	Solvent	τ(Au–CH_3),[a] ppm	$^3J(^{31}P\text{–}H)$, Hz
cis-$(CH_3)_2AuClP(C_6H_5)_3$	CCl_4	9.28 (0.99 ± 0.1)	8.5
		8.67 (1)	9.3
$(CH_3)_3AuP(C_6H_5)_3$	CCl_4	10.09 (2.0 ± 0.2)	7.1
		8.97 (1)	9.4
	C_6H_6	9.50 (1.98 ± 0.07)	7.1
		8.36 (1)	9.5
$(CH_3)_3AuP(C_2H_5)_3$	CCl_4	10.06 (1.99 ± 0.05)	6.7
		9.32 (1)	9.2
$(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$	CCl_4	9.96 (0.90 ± 0.02)	9.3
		9.71 (1)	8.2

[a] Relative integrated intensities in parentheses. Errors are estimated from four integrations and the relations for the propagation of variance.

Vibrational Spectra.—The infrared intensities of gold–carbon bond stretching vibrations of the dimethyl compounds are usually very low.[8–10] As noted above, with a ligand such as triphenylphosphine present, in-

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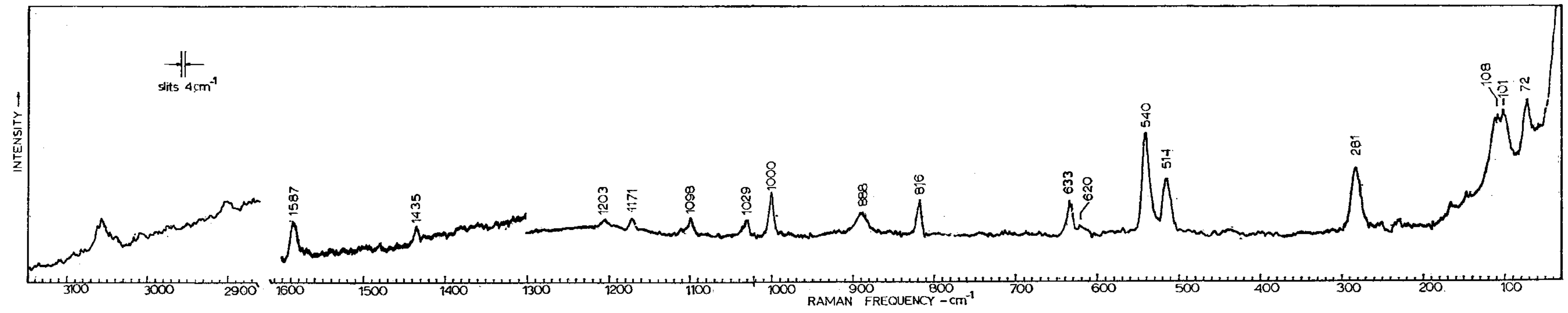

Figure 1.—Laser Raman spectrum of $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ excited with a He–Ne laser. Bands are labeled with the Raman shifts in cm^{-1}. Scan conditions: slits, 4 cm^{-1}; scan rate, 10 cm^{-1} min^{-1}; period, 2 sec.

TABLE II

RAMAN SPECTRA OF $(CH_3)_2AuYP(C_6H_5)_3$ ($Y^- = Cl^-, CH_3^-, \sigma\text{-}C_5H_5^-$)[a]

$\nu[(CH_3)_2AuClP(C_6H_5)_3]$	$\nu[(CH_3)_3AuP(C_6H_5)_3]$			$\nu[(\sigma\text{-}C_5H_5)(CH_3)_2AuP(C_6H_5)_3]$	$\nu[(\sigma\text{-}C_5H_5)_2Hg]$[11]	Qualitative assignment
Powder	Powder	CS_2 soln	CCl_4 soln	Powder		
				72 m		Skeletal modes
				100 s		
				108 s		
159 m, b			160 w			$\delta(AuC_3) + \nu(Au\text{–}P)$
	256 m	255 m	255 m			
				281 vs	321 s	Ring–metal str
281 m, b						$\nu(Au\text{–}Cl) + \delta(AuC_2)$
300 w, sh						
430 vw	434 vw			434 vw		$P(C_6H_5)_3$
542 vs	511 vs	510 vs, p[b]	509 vs	514 vs		$\nu(Au\text{–}C)$
549 vs	544 vs	543 vs, p[c]	544 vs	540 vs		
621 w	618 w	d	621 w			$P(C_6H_5)_3$
				633 s	639 s	$\sigma\text{-}C_5H_5$
690 w	694 w	d	689 vw			$P(C_6H_5)_3$
712 w	705 w					
				816 vs	815 s	$\sigma\text{-}C_5H_5$
				894 s, vb	874 s	$\sigma\text{-}C_5H_5$
1005 s	1002 s	1000 s	1000 s	1000 s		$P(C_6H_5)_3$
1027 m	1028 m	1028 m	1027 m	1029 m		$P(C_6H_5)_3$
1099 m	1100 m	1100 m	1100 m	1098 m		$P(C_6H_5)_3$
1161 w	1160 w					$P(C_6H_5)_3$
1188 m	1175 m	1173 m	1180 m	1171 m		$\delta_s((CH_3)Au)$
1240 w	1211 m	1209 m	1210 m	1208 m		
				1435 w	1445 m	$\sigma\text{-}C_5H_5$
1575 w	1573 w, sh					$P(C_6H_5)_3$
1589 m	1587 m	1595 m	1589 m	1587 w		$P(C_6H_5)_3$
2898 m	2893 w, b	e	2896			$\nu((C\text{–}H)AuCH_3)$
f	f	e	2902 m	2900 w		
3059 m, b	3056 m, b	e	3059 m, b	3030–3100 m, vb		$\nu((C\text{–}H)P(C_6H_5)_3)$, $\nu((C\text{–}H)C_5H_5)$

[a] Values are in reciprocal centimeters. Abbreviations: v, very; s, strong; m, medium; w, weak; b, broad; sh, shoulder. [b] Depolarization ratio $\rho = 0.36$. [c] Depolarization ratio $\rho = 0.58$. [d] Obscured by solvent. [e] Region not examined. [f] A Lyman ghost appears in this region with powder samples.

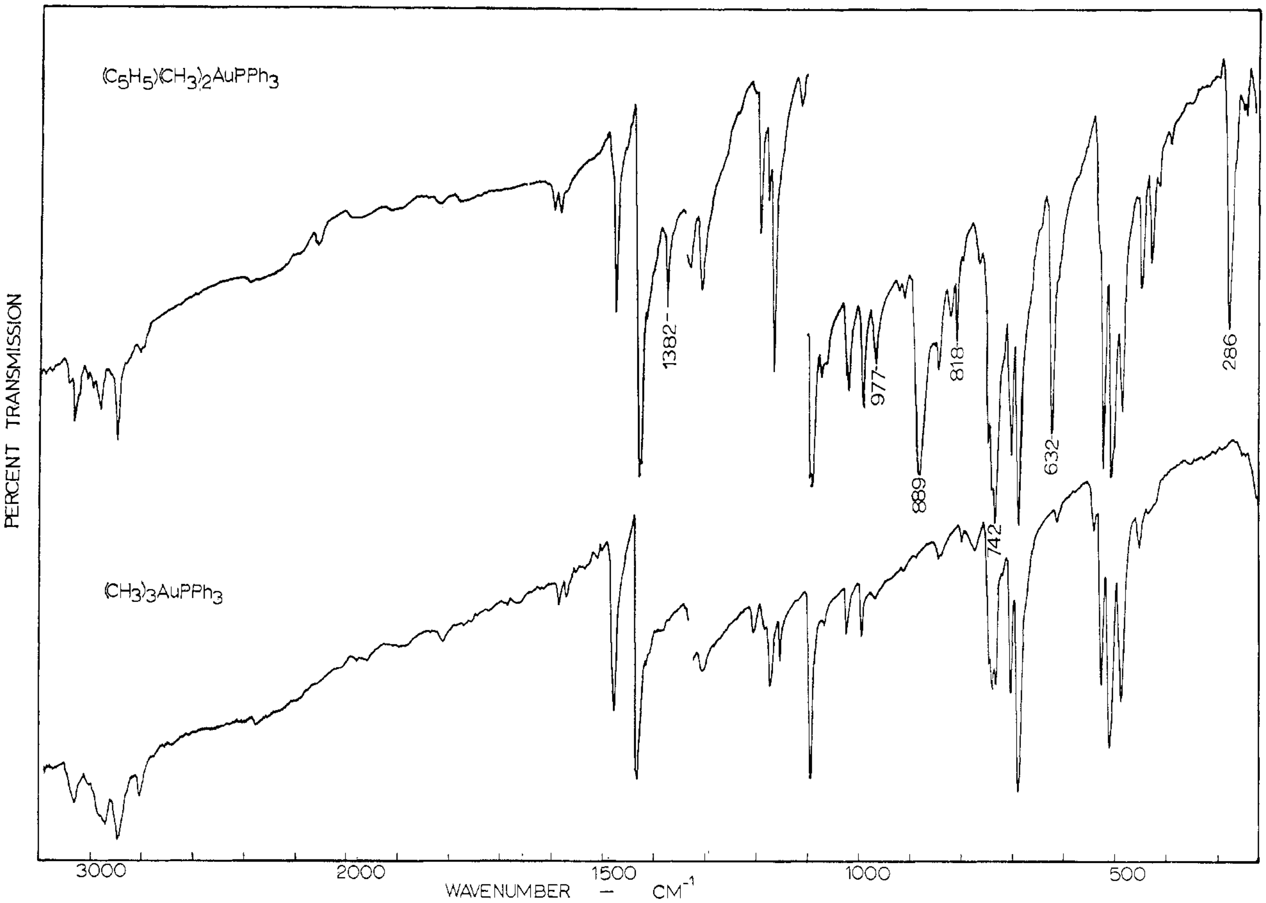

Figure 2.—Infrared spectra of $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ and $(CH_3)_3AuP(C_6H_5)_3$ recorded with split mulls—Halocarbon, KBr plates and Nujol, CsI plates.

frared spectra are of limited usefulness in discussing the skeletal structure and bonding. Conversely Au–C stretching vibrations have high Raman intensities. In addition, the low-frequency vibrations of the phenyl groups have low Raman intensities, and, for the most part, they do not interfere with the assignment of the skeletal vibrations. This is best illustrated by a comparison of the Raman and infrared spectra of $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$, Figures 1 and 2. The discussion of the structures and bonding trends of these compounds which follows is based primarily on the pmr and Raman spectra.

The Raman frequencies of $(CH_3)_2AuClP(C_6H_5)_3$, $(CH_3)_3AuP(C_6H_5)_3$, and $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ together with the corresponding frequencies of $(\sigma\text{-}C_5H_5)_2Hg$[11] are collected in Table II.

The assignments of the bands to internal vibrations of the triphenylphosphine portion of these molecules are straightforward and were made by comparison with the Raman spectrum of $P(C_6H_5)_3$. Many workers have examined the vibrations of $P(C_6H_5)_3$, and there are four studies of the Raman spectrum.[12–15] Deacon and Green[15] have discussed the metal-sensitive modes and how they shift upon coordination. The Raman spectra both for the crystalline powder and solutions of $(CH_3)_3AuP(C_6H_5)_3$ are illustrated in Figure 3. The chloride complex $(CH_3)_2AuClP(C_6H_5)_3$ serves as a model compound for the assignment of the coordinated phosphine vibrations, and its Raman spectrum below 1600 cm^{-1} and that of $P(C_6H_5)_3$ are illustrated in Figure 4. Infrared spectra of $(CH_3)_2AuClP(C_6H_5)_3$ and $P(C_6H_5)_3$ are illustrated in Figure 5. Obviously these are much less use than the Raman spectra for determining the skeletal vibrational frequencies.

Some of the infrared bands due to the coordinated cyclopentadienyl group can be identified by comparison of the spectrum of $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ with that of $(CH_3)_3AuP(C_6H_5)_3$, although most of the weak bands are masked by the $P(C_6H_5)_3$ absorptions. This is illustrated in Figure 2, where the frequencies involving the C_5H_5–Au group are indicated.

Because of the difficulties in the assignments of the AuC_3 stretching vibrations in the infrared spectra of $(CH_3)_3AuP(C_6H_5)_3$, Raman and infrared spectra also were obtained for $(CH_3)_3AuP(C_2H_5)_3$ where the phosphine interferes less. The infrared spectrum has been reported earlier.[5] These are collected in Table III. The Raman spectrum also is illustrated in Figure 4 and the infrared spectrum in Figure 5.

Again it is considerably easier to assign the Raman spectrum because it appears that the ethyl groups of $P(C_2H_5)_3$ contribute only very weak scattering. Spectra have been reported for the free ligand[16] and recently

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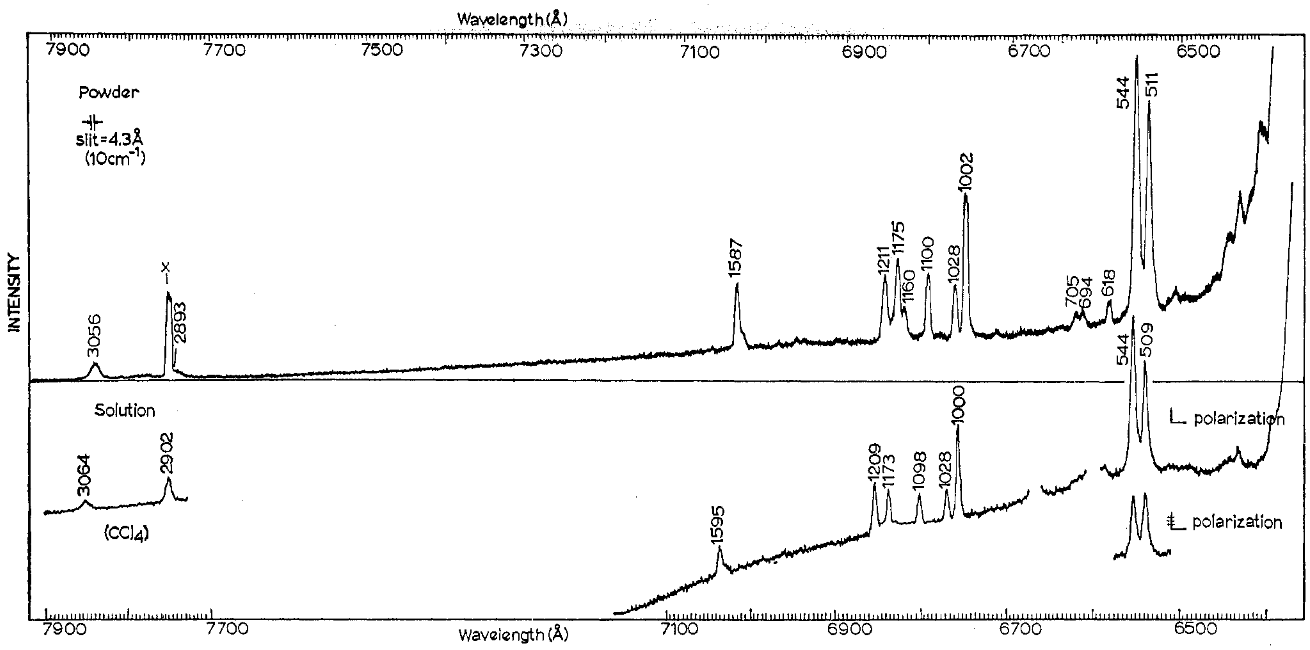

Figure 3.—Laser Raman spectrum of $(CH_3)_3AuP(C_6H_5)_3$ excited with an He–Ne laser. Bands are labeled with the Raman shifts in cm^{-1}. Scan conditions for both powder and solution: slits, 4.3 Å (*ca.* 9.6 cm^{-1}); scan rate, *ca.* 30 cm^{-1} min^{-1}; period, 2 sec.

TABLE III

RAMAN AND INFRARED SPECTRA OF LIQUID $(CH_3)_3AuP(C_2H_5)_3$ BELOW 1300 CM^{-1} [a]

ν, cm^{-1}		
Raman	Infrared	Qualitative assignments
289 m		$\delta(AuC_3) + \nu(AuP)$
327 w, sh	335 m	$P(C_2H_5)_3$
368 vs		$P(C_2H_5)_3$
513 vs	504 m	$\nu(AuC_3)$
540 vs	545 m	
642 w	640 w	$\nu(C–P)$
	750 vs, vb	$\rho_r(H_3C–Au)$, CH_2 rock $(P–CH_2)$
987 vw		$P(C_2H_5)_3$
1040 w, vb	1044 vs, vb	$P(C_2H_5)_3$
1176 m	1180 m	$\delta_s(CH_3–Au)$
	1191 w	$P(C_2H_5)_3$
1208 m	1213 m	$\delta_s(CH_3–Au)$
	1261 m	$P(C_2H_5)_3$
1380 w		$P(C_2H_5)_3$
1420 w		$P(C_2H_5)_3$
1460 w		$P(C_2H_5)_3$

[a] For abbreviations see Table II.

for the bound ligand in some platinum(II) complexes.[17] Only two sharp Raman signals are observed in the methyl deformation region at 1176 and 1208 cm^{-1} compared to 1175 and 1211 cm^{-1} for $(CH_3)_3AuP(C_6H_5)_3$. Two very intense bands are observed at 513 and 540 cm^{-1} clearly assignable to gold–carbon stretching, and these may be compared with the intense bands at 511 and 544 cm^{-1} with $(CH_3)_3AuP(C_6H_5)_3$. The vibrations of all of these compounds below 350 cm^{-1} are likely to be complex motions involving Au–P stretching and skeletal deformations.

The infrared spectrum of $(CH_3)_3AuP(C_2H_5)_3$ shows two bands at 504 and 545 cm^{-1}, and Coates and Parkin[5] previously have assigned such infrared bands to AuC_3 stretching. It is clear that while the intensities of the gold–carbon stretching vibrations of the dimethylgold halides are so low as to be almost undetectable,[8–10] this is not true for the trialkylgold compounds. Here these stretches have medium intensities. Nevertheless, it appears that the intense bands in the 500–600-cm^{-1} region of the $P(C_6H_5)_3$ compounds are due to the phosphine and that they mask the gold–carbon vibrations in the infrared spectra. At higher frequencies, the methyl and methylene groups of the triethylphosphine ligand give such intense infrared absorptions that no meaningful assignment can be made from the infrared data alone.

Discussion

The alkylation of $AuBr_3$[4] or of $[(CH_3)_2AuBr]_2$[4] in diethyl ether gives quite low yields of trimethylgold(III) even when the product is isolated immediately as the triphenylphosphine adduct.[5] For example, the methylation of $AuBr_3$ followed by the addition of triphenylphosphine led to the reduction of 47% of the gold to the metal.[5] No reduction to gold metal was observed when crystalline $(CH_3)_2AuIP(C_6H_5)_3$ was dissolved in ether and alkylated, reaction 1. A similar

$$(CH_3)_2AuIP(C_6H_5)_3 + CH_3Li \xrightarrow{(C_2H_5)_2O} (CH_3)_3AuP(C_6H_5)_3 + LiI \quad (1)$$

reaction was employed to prepare $(CH_3)_3AuP(C_2H_5)_3$. In this case both the product and $(CH_3)_2AuIP(C_2H_5)_3$ are liquids at room temperature.

This general reaction was employed in the synthesis of the mixed cyclopentadienyldimethyl derivative. This compound appears to be stable at room temperature for long periods of time. Because of the presence of the two methyl groups and the triphenylphosphine which leads to low molecular symmetry, the pmr spectrum is consistent only with a nonrigid cyclopentadienyl group where the protons become equivalent *via* an intramolecular process. This could be rotation about the ring normal of a pentahapto ring or hopping of the metal in a less symmetric fluxional structure.

The principal structures which might be considered for $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ are the π bonded (pentahapto), the π allyl (trihapto), and the σ bonded (mono-

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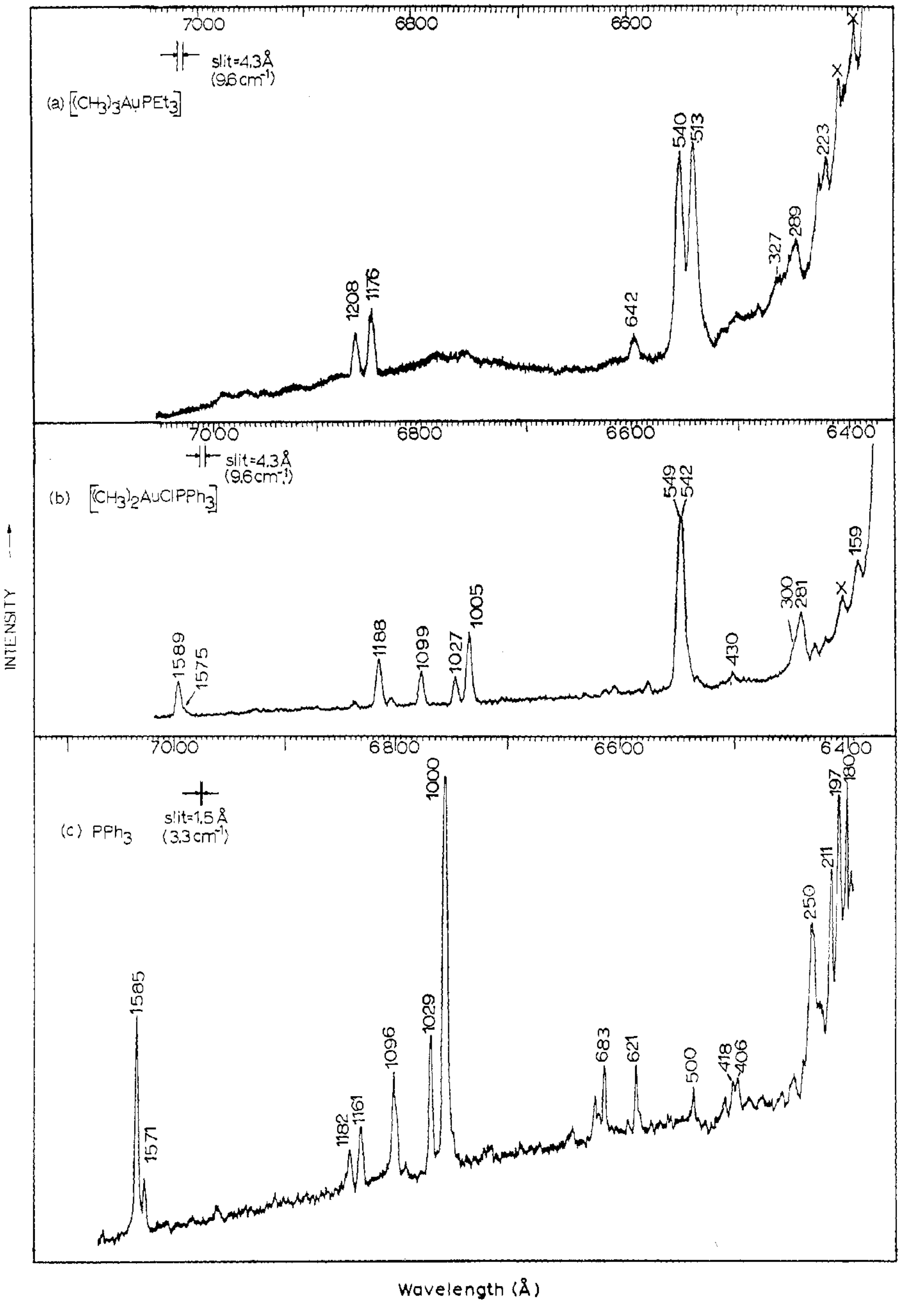
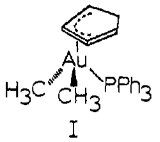


Figure 4.—Laser Raman survey spectra (100–1500 cm^{-1}) of (a) $(CH_3)_3AuP(C_2H_5)_3$, (b) $(CH_3)_2AuClP(C_6H_5)_3$, and (c) $P(C_6H_5)_3$. Ghosts are marked with X. Bands are labeled with the Raman shifts in cm^{-1}. Scan conditions were optimized for each compound, and this accounts for the slight differences in the display.

hapto). Kitching and Hegarty[18] have summarized the nmr behavior to be expected at different temperatures with these modes of binding in bis(cyclopentadienyl)-mercury. The behavior should be more complicated for $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ where the low molecular symmetry would be expected to lead to more than one cyclopentadienyl proton resonance at low temperature even with a pentahapto structure.

Considering the electronic configuration of gold and the noble gas formalism, it is difficult to conceive of any stable structure with a pentahapto ring as well as the coordinated phosphine. The $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ showed no tendency to lose $P(C_6H_5)_3$ which would give the analog of $(\pi\text{-}C_5H_5)(CH_3)_3Pt$.[19] The nmr spectra show no line broadening at room temperature such as has been observed as a result of exchange of the neutral ligand L in $[(CH_3)_2AuLCl]$[20] complexes.



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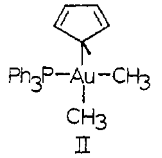

II

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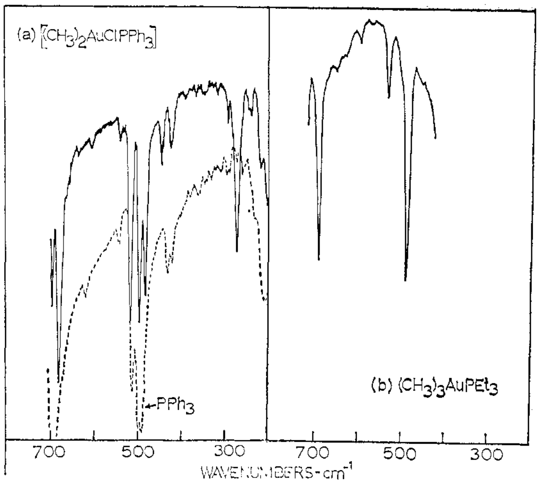

Figure 5.—Infrared spectra of (a) $(CH_3)_2AuClP(C_6H_5)_3$ and $P(C_6H_5)_3$ (broken line) as Nujol mulls and (b) $(CH_3)_3AuP(C_2H_5)_3$ as the neat liquid.

A fluxional trihapto complex, structure I, would give an 18-electron configuration about gold. With the fluxional cyclopentadienyl group, it is likely that the methyl protons would give a single resonance at room temperature contrary to what is observed; however it is not possible to exclude completely the trihapto structure on the basis of the nmr spectrum. A fluxional σ-bonded structure, II, with the cyclopentadienyl group bond trans to a methyl is consistent with the spectra. The presence of appreciable amounts of the trans isomer can be ruled out on the basis of the two methyl proton resonances observed in the nmr spectrum.

The Raman spectrum of $(CH_3)_2AuClP(C_6H_5)_3$ provides an example for the vibrations of $P(C_6H_5)_3$ coordinated in an organogold(III) complex. As may be seen from the data in Table II, these frequencies are very similar in $(CH_3)_2AuClP(C_6H_5)_3$, $(CH_3)_3AuP(C_6H_5)_3$, and $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$. In the infrared spectra, the very intense absorptions of $P(C_6H_5)_3$ tend to obscure the vibrations of the $(CH_3)_3Au$ and $(C_5H_5)(CH_3)_2Au$ moieties.

The Raman spectrum of $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ provides sufficient information to rule out a pentahapto cyclopentadienyl ring. As discussed by Cotton and Marks[21] for the infrared spectra of pentahapto and monohapto groups, the vibrational spectrum of a monohapto ring (C_s) should be much more complex than that of a pentahapto ring (C_{5v}). Lippincott and coworkers[22,23] have reported the Raman spectrum of $(\pi\text{-}C_5H_5)NiNO$, and one intense band was observed at 1114 cm^{-1} together with weak bands at 1060, 961, 840, and 810 cm^{-1}. In contrast, Maslowsky and Nakamoto[11] found that σ-bonded cyclopentadienyl groups of $(\sigma\text{-}C_5H_5)_2Hg$ gave strong to medium Raman bands at 1445, 1420, 1384, 1109, 874, 815, and 639 cm^{-1}. Raman bands were observed for the cyclopentadienyl group of $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ at 1435, 894, 816, and 633 cm^{-1}. The band expected at *ca.* 1100 cm^{-1} appears to occur as a shoulder at *ca.* 1110 cm^{-1} on the metal-sensitive band of $P(C_6H_5)_3$ which is observed at 1098 cm^{-1}. Infrared bands which result from the $(C_5H_5\text{–}Au)$ portion of the molecule were observed at 1382 (m), 977 (m), 889 (vs), 818 (m), 742 (vs), 632 (vs), and 286 cm^{-1} (vs). These infrared data are similar to the frequencies of $(\sigma\text{-}C_5H_5)_2Hg$[11] and consequently are suggestive of a monohapto structure, although they are by no means conclusive. Together the Raman and infrared data exclude the pentahapto structure, but it is possible that the low-symmetry trihapto structure might give frequencies similar to those observed.

The Au–C skeletal stretching frequencies also provide information on the bonding. With only two methyl groups in the gold coordination sphere, *e.g.*, $(CH_3)_2AuClP(C_6H_5)_3$, coupling between the two orthogonal Au–C coordinates through the heavy gold atom is very slight. The two bands at 542 and 549 cm^{-1} were not even resolved under the conditions used in recording the survey spectrum illustrated in Figure 4 (10-cm^{-1} slits). Slits of the order of 1 cm^{-1} were necessary to resolve them completely. The Raman activity of both modes confirms the cis arrangement of the methyl groups. Both are also infrared active; however no vibrations corresponding to these were found above the noise level in the infrared spectrum consistent with the very low infrared intensities observed for other cis dimethylgold compounds.

To a first approximation, the skeletal vibrations of $(CH_3)_3AuP(C_6H_5)_3$ and $(CH_3)_3AuP(C_2H_5)_3$ should behave according to the selection rules of the C_{2v} point group. With these compounds, one Au–C internal stretching coordinate is orthogonal to the other two. The Au–C stretching vibration of the methyl group trans to the phosphine would be expected to be almost independent of those of the mutually trans methyl groups. Because of the low symmetry, all three stretches should be both Raman and infrared active for all of the triorgano compounds. Only two polarized bands were observed with the trimethyl compounds in the Raman spectrum and two bands in the infrared spectrum. The trans methyl groups seem to give intensities similar to linear $(CH_3)_2M^{z+}$ ions.[24] Qualitative descriptions of the normal modes of the trimethyl compounds are given in Figure 6. The strong trans influence of the methyl groups leads to a marked decrease in frequency for the stretching of the mutually trans Au–C bonds. Also the similarity of the higher frequency Au–C stretch to the stretching frequencies of $(CH_3)_2AuClP(C_6H_5)_3$ suggest that the third alkyl group leads to very little change in the Au–C bond trans to the phosphine.

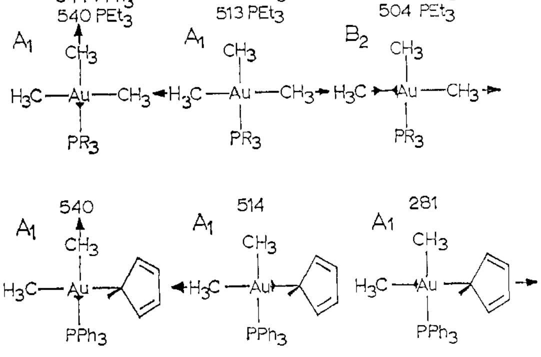

Figure 6.—Symmetry modes for the trialkylgold complexes.

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The gold–ring stretching vibration of $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ clearly is assignable to the intense Raman and infrared bands observed at 281 and 286 cm^{-1}, respectively. From the Raman spectra it is found that substitution of C_5H_5 for CH_3 only shifts the higher frequency Au–C stretch from 544 to 540 cm^{-1} and the lower frequency vibration from 511 to 514 cm^{-1}. Such small shifts indicate that the electron distribution about gold is very similar in $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ and $(CH_3)_3AuP(C_6H_5)_3$. Consequently a monohapto cyclopentadienyl group is indicated. If the ring were trihapto, the change from a one- to a three-electron donor would be expected to lead to a decrease in the Au–CH_3 stretching frequencies. Similar arguments have been advanced against the π-allylic structure for $(C_5H_5)_2Hg$.[18] Qualitative descriptions of the normal Au–C stretching modes for $(C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ also are given in Figure 6.

No bands were observed in these compounds above 300 cm^{-1} which could be assigned to gold–phosphorus bond stretching. It is to be expected that these vibrations will be mixed appreciably with the skeletal deformations in the range 200–300 cm^{-1}.

In formal sense, $(\sigma\text{-}C_5H_5)(CH_3)_2AuP(C_6H_5)_3$ and the recently reported $(\sigma\text{-}C_5H_5)(CH_3)_2Tl$[25,26] are analogous, since both have a σ-bonded cyclopentadienyl group and 16 electrons about the metal. As expected, the thallium compound forms adducts to give an 18-electron configuration, while the gold compound shows no signs of this. The thallium compound undergoes intermolecular exchange of the cyclopentadienyl groups as indicated by the collapse of the ^{203}Tl- and ^{205}Tl–cyclopentadienyl proton spin–spin coupling. Coupling with ^{31}P in the gold compound gives a sharp doublet for the cyclopentadienyl protons at 40° with an averaged coupling constant of 2.8 Hz indicating that an intramolecular process causes the collapse of the different σ-cyclopentadienyl proton resonances.

In summary, $(CH_3)_2AuClP(C_6H_5)_3$ undergoes substitution reactions of the chloride very much like Cl–Au–$P(C_6H_5)_3$. The methyl groups are inert in many reactions and increase the electron density at gold very much above that suggested by the formal trivalent oxidation state. The bonding of the cyclopentadienyl group in cyclopentadienyl(triphenylphosphine)gold(I)[27] may be similar to that of $(\sigma\text{-}C_5H_5)(CH_3)_2AuP(C_6H_5)_3$, although the mode of bonding of the cyclopentadienyl ligand in the gold(I) complex does not seem to have been investigated.

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Metallocycles Involving Two 1,2-*Dihapto*pyrazolide Bridges

BY S. TROFIMENKO*

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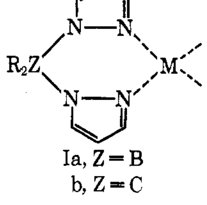
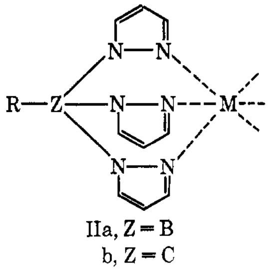
Stable, nonplanar metallocycles of structure $L_2M(pz)_2ML_2$ containing two 1,2-*dihapto*pyrazolide (or substituted pyrazolide) ligands bridging the two metals have been prepared. Examples include M = Rh (L = CO and L_2 = 1,5-cyclooctadiene) and M = Pd (L_2 = π-allyl or 2-substituted π-allyl and L_2 = 1-*N*-dihapto-2-(diethylaminomethyl)phenyl). Nmr spectra of the π-allyl group indicate stereochemical nonrigidity.

The coordination chemistry of pyrazole and of some of its derivatives is not well established. Only a few transition metal complexes containing a 2-*monohapto*-pyrazole ligand have been reported.[1-3] These complexes, similar to those formed by pyridine, are of the general type M(2-*hapto*pyrazole)$_n$X$_2$ where n = 4 or 6 and X is a univalent anion. The 2-hapto structure in these compounds and hydrogen bonding to X (when X = halogen) have been established by extensive X-ray studies.[4-9]

A variety of chelating systems derived from pyrazolide ion are also known. For instance, when two pyrazolyl rings are linked by an R_2B group (Ia), the resulting dipyrazolylborate ion represents an extensive new class of ligands[10] which form neutral compounds with divalent transition metal ions. Ligands Ia and IIa also possess a wealth of organometallic chemistry.[11-13]



Ia, Z = B
b, Z = C



IIa, Z = B
b, Z = C

When the bridging group is carbon instead of boron, the resulting polypyrazolylalkanes Ib and IIb, which

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