The gold–ring stretching vibration of $(C_5H_5)(CH_3)_2$-$AuP(C_6H_5)_3$ 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,

(25) A. G. Lee and G. M. Sheldrick, *Chem. Commun.*, 441 (1969).
(26) A. G. Lee, *J. Chem. Soc. A*, 2157 (1970).

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.

(27) R. Hüttel, U. Rafaay, and H. Reinheimer, *Angew. Chem., Int. Ed. Engl.*, **6**, 862 (1967).

---

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

BY S. TROFIMENKO*

Stable, nonplanar metallocycles of structure L$_2$M(pz)$_2$ML$_2$ 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 $M(2\text{-}hapto\text{pyrazole})_n X_2$ 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$_2$B group (Ia), the resulting dipyrazolylborate ion represents an extensive new class



Ia, Z = B
b, Z = C

IIa, Z = B
b, Z = C
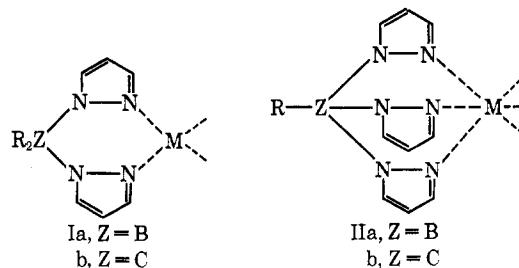
of ligands[10] which form neutral compounds with divalent transition metal ions. Ligands Ia and IIa also possess a wealth of organometallic chemistry.[11–13]

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

* Plastics Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del. 19898.

(1) M. Inoue, M. Kishita, and M. Kubo, *Inorg. Chem.*, **4**, 626 (1965).
(2) N. A. Daugherty and J. H. Swisher, *ibid.*, **7**, 1651 (1968).
(3) D. R. Crow, *J. Polarogr. Soc.*, **11**, 67 (1965).
(4) C. W. Reiman and A. D. Mighell, *J. Phys. Chem.*, **71**, 2375 (1967).
(5) C. W. Reiman, A. D. Mighell, and F. A. Mauer, *Acta Crystallogr.*, **23**, 135 (1967).
(6) A. D. Mighell, C. W. Reiman, and A. Santoro, *ibid.*, *Sect. B*, **25**, 595 (1969).
(7) C. W. Reiman, A. Santoro, and A. D. Mighell, *ibid.*, *Sect. B*, **26**, 521 (1970).
(8) C. W. Reiman, *Chem. Commun.*, 146 (1969).
(9) C. W. Reiman, *J. Phys. Chem.*, **74**, 561 (1970).
(10) These also include uninegative tridentates such as IIa: S. Trofimenko, *J. Amer. Chem. Soc.*, **89**, 3170, 6288 (1967).
(11) S. Trofimenko, *ibid.*, **91**, 588 (1969).
(12) S. Trofimenko, *ibid.*, **90**, 4754 (1968).
(13) S. Trofimenko, *Inorg. Chem.*, **8**, 2675 (1969).

are isosteric and isoelectronic with the polypyrazolyl-borates, exhibit similar coordination chemistries. The main difference is that ligands Ib and IIb are neutral and hence their complexes bear a higher charge (greater by 1+ per ligand).[14]

In the above systems the metal is coordinated to pyrazolyl nitrogens exclusively. Another class of ligands is suitably 1-substituted pyrazoles which act as bidentates, with the 2 nitrogen and a heteroatom on the 1 substituent coordinating to the metal. The polymeric complexes derived from 1-pyrazoledithiocarboxylate ion[15] (III) and those based on, *e.g.*, hexafluoroacetone[16] (IV) are examples.



III IV
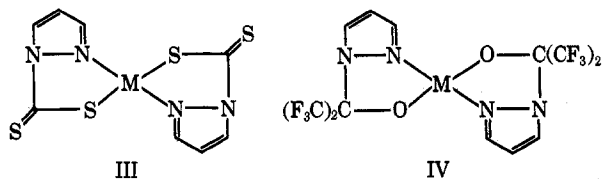
By contrast, little is known about the coordination behavior of pyrazolide ion itself. This ion, V, possesses



V



VI
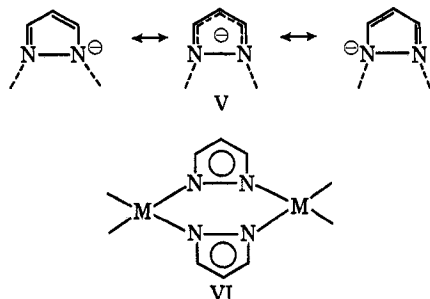
$C_{2v}$ symmetry and would be expected to maintain this symmetry when acting as a uninegative 1,2-dihapto ligand. Since coordination of the same metal ion to both nitrogens is impossible because of molecular geometry, the driving force for chelation should favor the formation of metallocycles of general structure VI. Molecular models indicate these rings to be puckered (boat form) rather than planar ($C_{2v}$ rather than $D_{2h}$ symmetry). In a suitable system the two metals could be bridged by a third 1,2-*dihapto*pyrazolide ligand, as in the triptycene-like anion VII whose $D_{3h}$ symmetry has been supported by nmr.[17]

However, without "end-capping" groups on the metal, 1,2-*dihapto*pyrazolides of transition metals form a polymeric chain[1,18,19] (VIII), the metal being sometimes coordinated to additional ligands such as water or ammonia.
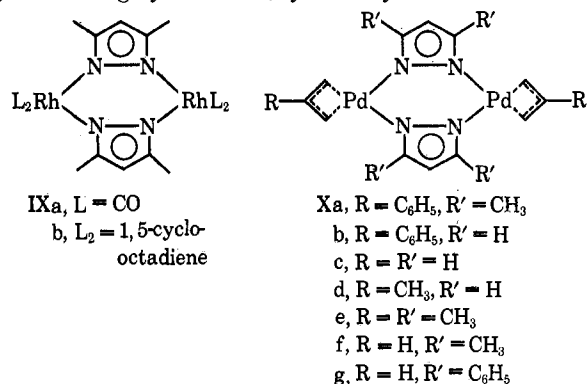


VII VIII
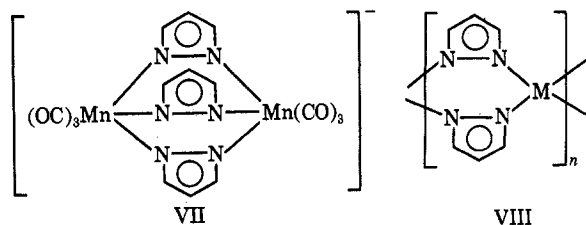
To synthesize monomeric transition metal compounds having the metallocycle structure VI, metals preferring four-coordination and containing two blocking ligands
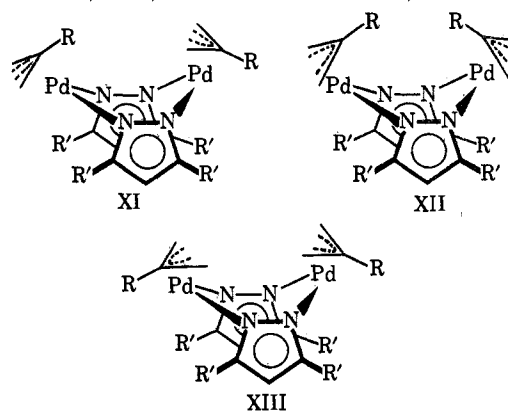
were used. Thus the reaction of 3,5-dimethylpyrazolide ion with $[(OC)_2RhCl]_2$ gave a quantitative yield of a yellow solid which was assigned structure IXa, as its nmr spectrum showed all methyl groups to be spectroscopically equivalent and the molecule to be of $C_{2v}$ symmetry. Similarly, $[(1,5-cyclooctadiene)RhCl]_2$ was quantitatively converted to the thermally stable (up to 270°) compound IXb. Its nmr spectrum confirmed the presence of both ligands, again indicating overall $C_{2v}$ symmetry for the molecule.

That the 1,5-cyclooctadiene ligand is not sterically very demanding follows from the nmr spectrum of $HB(3,5-(CH_3)_2pz)_3Rh(1,5-cyclooctadiene)$ where all three 3,5-dimethylpyrazolyl groups are spectroscopically equivalent and thus are exchanging rapidly at room temperature.[20]

Another family of metallocycles was derived from various palladium precursors. For instance, the reaction of 3,5-dimethylpyrazolide ion with $(\pi-CH_2CC_6-H_5CH_2PdCl)_2$ yielded a colorless solid with correct elemental analysis and molecular weight for structure Xa. Its nmr spectrum, while showing the correct proton ratios for both ligands, was more complex than would be expected from a molecule of static or dynamic $C_{2v}$ symmetry: the syn and anti hydrogens showed up as two peaks each, with a separation of only 3 Hz for syn and 43 Hz for anti. The methyl groups were also nonequivalent ($\Delta = 21$ Hz). On heating to 167° the limiting[21] high-temperature spectrum was obtained (Figure 1a) indicating dynamic $C_{2v}$ symmetry for the molecule.



IXa, L = CO
b, $L_2$ = 1,5-cyclooctadiene

Xa, R = $C_6H_5$, R' = $CH_3$
b, R = $C_6H_5$, R' = H
c, R = R' = H
d, R = $CH_3$, R' = H
e, R = R' = $CH_3$
f, R = H, R' = $CH_3$
g, R = H, R' = $C_6H_5$

Three conformational isomers are possible for structures X: XI, XII, and XIII. Of these, structure XI



XI XII



XIII

(14) S. Trofimenko, *J. Amer. Chem. Soc.*, **92**, 5118 (1970).
(15) S. Trofimenko, *J. Org. Chem.*, **33**, 890 (1968).
(16) W. Mahler, U. S. Patent 3,265,705 (Aug 9, 1966).
(17) S. Trofimenko, *J. Amer. Chem. Soc.*, **91**, 5410 (1969).
(18) R. T. Pflaum and L. H. Dieter, *Proc. Iowa Acad. Sci.*, **64**, 235 (1957).
(19) S. Trofimenko, unpublished work.

(20) The nmr spectrum would also be consistent with a five-coordinate Rh where either one of the ligands is rotating rapidly around the B–Rh axis. Such a rotation must be taking place in any event since otherwise the three 3,5-dimethylpyrazolyl groups would not become equivalent.

(21) The anti proton singlet was not very sharp yet, but at higher temperatures deposition of palladium in this and in other compounds became appreciable.
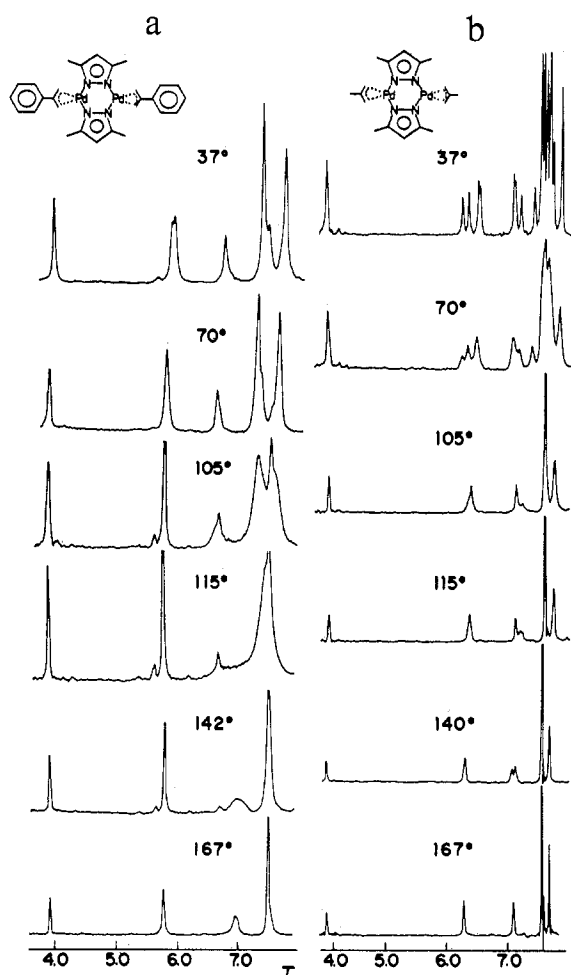
Figure 1.—The temperature-dependent nmr spectra ($\pi$-allyl region only) of (a) bis(1,2-*dihapto*-3,5-dimethylpyrazolido)dipalladium bis($\pi$-(2-phenyl)allyl) and (b) bis(1,2-*dihapto*-3,5-dimethylpyrazolido)dipalladium bis($\pi$-(2-methyl)allyl).

has each set of syn and anti H's in a different environment and the left and right set of R' groups should be spectroscopically nonidentical. By contrast, structures XII and XIII are both of $C_{2v}$ symmetry. The room-temperature spectrum of Xa would be compatible with either XI or a 1:1 mixture of XII and XIII. The former possibility looks more attractive by (a) analogy to the known [($\pi$-allyl)Pd(OAc)]$_2$ where a structure analogous to XI was established by an X-ray study,[22] (b) the possibility that steric interactions between the R groups would render structure XII incapable of existence, and (c) the probability that even if structure XII were capable of existence, it is unlikely that it would exist in exactly a 1:1 ratio with XIII. Assuming, then, Xa to possess structure XI, its stereochemical nonrigidity may be ascribed to simple rotation of the $\pi$-allyl groups, ample precedents for which are known.[23,24] While the same results would be obtained from rapid inversions of the whole molecule, as has been suggested[25] for [($\pi$-allyl)Pd(OAc)]$_2$, such a mechanism seems unlikely as the planar transition state for such an inversion would seem to entail prohibitive steric strain and thus

be energetically unfavorable with respect to the simple rotational process.

A number of other metallocycles of structure X was prepared varying the substituents R and R'. They were white solids of fairly high thermal stability, some of which had good solubility in organic solvents. The related compound Xb was also fluxional; *i.e.*, the syn and anti H's appeared as two pairs of singlets which coalesced to two singlets at 167°. This time, however, $\Delta_{syn}$ and $\Delta_{anti}$ were closer (3 and 8 Hz, respectively). It appears that the anti H's are more sensitive to 3,5 substituents than the syn.

The least sterically hindered system should be Xc where both R and R' are hydrogen and steric interactions should be minimal. Indeed, the room-temperature nmr spectrum of Xc showed a normal $\pi$-allyl pattern. Introduction of a methyl on the central $\pi$-allyl carbon as in Xd produced a spectrum where the syn and anti H's were still sharp singlets, but two different methyl groups were observed ($\Delta_{CH_3}$ = 5 Hz).

A very complicated yet clean pattern was obtained for Xe (see Figure 1b). There, apart from a complex methyl region, four types of syn and four of anti H's are discernible. On heating to 167° a sharp spectrum indicating dynamic $C_{2v}$ symmetry is observed. At 105° the pyrazolyl methyls are equivalent, the syn H's are close to equivalence, and one pair of anti H's has become equivalent, but the other anti peak is still quite broad. At 140° the anti H's are a doublet which, finally, at 167° sharpens to give the spectrum characteristic of dynamic $C_{2v}$ symmetry. The whole process is reversible and, on cooling, the original room-temperature spectrum is obtained. It would appear that in this case all three rotamers XI, XII, and XIII have long enough lifetimes to be observed simultaneously by nmr. It is possible that their interconversion may proceed along more than one pathway. In the absence of more structural data we are reluctant to speculate on the possible dynamic processes in operation, although presence of both rotation of $\pi$-allyl groups and inversion of the whole metallocycle may be possible.

The analogous compound with a simple $\pi$-allyl group Xf also seemed to contain all three isomers as judged by the presence of four methyl peaks and of very complex syn and anti multiplets. An even more complex and almost merging pattern of syn and anti hydrogens could be seen in Xg. However, at 140° the syn H's became a clean doublet ($J$ = 7.0 Hz) and the anti a pair of doublets ($J$ = 12 Hz, $\Delta$ = 3 Hz).
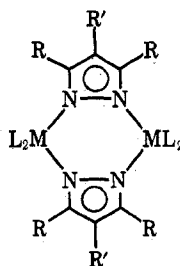
Another palladium metallocycle analogous to X was obtained from 3,5-dimethylpyrazolide ion and 2-(diethylaminomethyl)phenylpalladium(II) chloride dimer. The nmr spectrum of this compound shows two types of pyrazolyl methyls and two types of $N$-ethyl groups as well as two different benzylic H's. This would make the presence of *both* isomers XIV and XV not very likely since then four pyrazolyl methyls might be observable. The fact that benzylic hydrogens and ethyl groups are nonequivalent in this system stems from the puckered nature of the metallocycle. This does not, *per se*, distinguish between structures XIV and XV. Structure XIV is favored, however, since it seems to be the less sterically hindered one of the two, as the N-$(C_2H_5)_2$–CH$_3$ interaction can be reduced by a slight twisting of the pyrazolyl ring which would not be effec-

(22) M. R. Churchill and R. Mason, *Nature (London)*, **204**, 777 (1964).
(23) A. Davison and W. C. Rode, *Inorg. Chem.*, **6**, 2124 (1967).
(24) J. W. Faller and M. J. Incorvia, *ibid.*, **7**, 840 (1968).
(25) J. Powell, *J. Amer. Chem. Soc.*, **91**, 4311 (1969).

TABLE I
COMPOUNDS OF STRUCTURE



| $L_2$ | M | R | R' | Mp, °C | Yield, % | %C Calcd | %C Found | %H Calcd | %H Found | %M Calcd | %M Found | Nmr[a] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,5-Cyclooctadiene | Rh | CH₃ | H | 298–299 | 100 | 51.0 | 50.9 | 6.22 | 6.50 | 9.15 | 9.17 | (37°) s 4.51; m 5.2–5.9; m 6.7–8.3; s 7.58 (1:4:8:6) |
| (CO)₂ | Rh | CH₃ | H | 167–169 | 100 | 32.7 | 32.9 | 2.72 | 2.64 | 10.9 | 10.9 | (37°) s 4.20; s 7.70 (1:6) |
| π-2-Phenylallyl[c] | Pd | H | H | 213–215 | 89 | 49.6 | 49.7 | 4.14 | 4.06 | 9.66 | 9.77 | (37°) m 2.2–2.9; t (2.0) 3.71; s 6.10; s 6.15; s 6.83; s 6.96 (7:1:1:1:1:1) (140°) π-allyl region: s 6.05, broad "d" (half-height 11 Hz) 6.84 (167°) π-allyl region: s 6.05; s 6.84 (half-height 3.4 Hz) |
| π-2-Phenylallyl[d] | Pd | CH₃ | H | 173–175 | 98 | 52.8 | 52.6 | 5.03 | 5.07 | 8.80 | 8.86 | See Figure 1a |
| π-2-Methylallyl | Pd | H | H | 198–200 | 87 | 36.8 | 36.7 | 4.39 | 4.43 | 12.3 | 12.2 | (37°) 2d (overlap) 2.52; t (2.0) 3.70; s 6.52; s 7.14; s 7.84; s 7.92 (2:1:2:2:3) |
| π-2-Methylallyl | Pd | CH₃ | H | 178–180 | 92 | 42.2 | 41.9 | 5.48 | 5.50 | 10.9 | 10.8 | See Figure 1b |
| π-Allyl | Pd | H | H | ~190 dec | 79 | 33.5 | 33.4 | 3.72 | 3.74 | 13.5 | 13.1 | (37°) 2d (overlap) 2.44; t (2.0) 3.72; m 4.0–4.8; d (7.0) 6.25; d (12.2) 6.98 (2:1:1:1:2:2) |
| π-Allyl | Pd | CH₃ | H | ~200 dec | 84 | 39.5 | 39.6 | 4.94 | 5.00 | 11.9 | 11.7 | (37°) s 4.08; m 4.2–4.9; m 5.8–6.3; m 6.8–7.4; s 7.64; s 7.70; s 7.78; s 7.83 (1:1:2:2:3:3:3:3) |
| π-Allyl | Pd | H | Br[e] | 216–219 | 72 | 24.6 | 24.6 | 2.39 | 2.34 | 9.56 | 9.27 | b |
| π-Allyl | Pd | C₆H₅ | H | 239–241 dec | 85 | 59.0 | 59.1 | 4.37 | 4.29 | 7.65 | 7.64 | (37°) m 1.7–2.1; m 2.3–2.7; "d" (3.0) 3.3; m 4.7–5.4; m 6.6–7.3; m 7.4–8.3 (4:6:2:1:2:2) (140°) π-allyl region: m 4.5–5.1; d (7.0) 6.70; d (12.5) 7.47; d (12.5) 7.53 |
| π-Allyl | Pd | H | CN | 220 dec | 71 | 35.1 | 35.1 | 2.93 | 2.90 | 17.6 | 17.5 | b |
| 2-(Diethylaminomethyl)-phenyl | Pd | CH₃ | H | 211–215 | 78 | 52.9 | 52.9 | 6.34 | 6.46 | 11.6 | 11.5 | (37°) m 3.20; s 4.40; s 6.10; s 6.13; m 6.6–7.4; s 7.64; s 7.78; t (7.0) 8.53; t (7.0) 9.10 (4:1:1:1:4:3:3:3:3) |

[a] Listed are (temperature) multiplicity (*J*) τ (relative areas). The 37° spectra were measured in CDCl₃; those at higher temperatures, in *o*-dichlorobenzene. [b] Nmr spectra were not determined because of low solubility of these compounds. [c] Mol wt for this compound: calcd, 580; found (by osmometry in chloroform at 37°), 587. [d] Mol wt for this compound: calcd, 636; found (by osmometry in chloroform at 37°), 638. [e] Br analysis: calcd, 27.3%; found, 26.6%.



XIV



XV
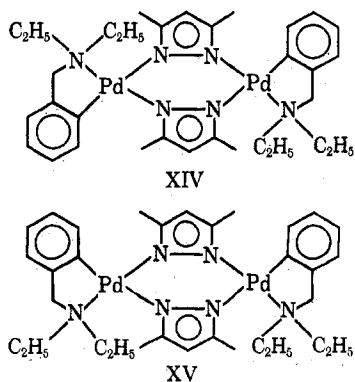
tive in structure XV. It is still difficult, in the absence of X-ray data, to make definitive structural predictions at this point.

As can be seen from the examples cited above, metallocycles based on the 1,2-*dihapto*pyrazolide ligand can be readily synthesized and possess good stability. No evidence of dissociation into monomeric fragments nor ring rupture by polar solvents has been observed, although these and other aspects of their chemistry were not investigated.

## Experimental Section

The various π-allylic palladium chloride dimers were prepared by published methods[26,27] as was the dimer of 1,5-cyclooctadienerhodium chloride.[28]

**Synthesis of Compounds IX and X.**—The same general method was used to synthesize the compounds listed in Table I. It consists of the reaction of a halogen-bridged binuclear species with pyrazolide ion as illustrated by one specific example.

**Bis(1,2-*dihapto*pyrazolido)bis-π-allyldipalladium(II).**—To 3.66 g of π-allylpalladium chloride dimer stirred in 20 ml of DMF was added 22 ml of a solution 1.0 *M* in pyrazole and 1.0 *M* in diisopropylethylamine. The yellow color of the solution was discharged rapidly. The solution was diluted with 400 ml of water and the product was extracted with methylene chloride. The extracts were washed several times with water to remove most of the DMF. The organic layer was separated and chromatographed on alumina, and the eluate was evaporated at reduced pressure. The residue was stirred with ether–hexane and filtered

(26) W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1585 (1964).
(27) J. K. Nicholson, J. Powell, and B. L. Shaw, *Chem. Commun.*, 175 (1966).
(28) R. B. King, *Organometal. Syn.*, **1**, 132 (1965).

yielding 3.4 g (79%) of white solid which was recrystallized from toluene. Its properties are listed in Table I.

**Hydrotris(3,5-dimethyl-1-pyrazolyl)borato(1,5-cyclooctadiene)-rhodium(I).**—A mixture of 5 mmol (as monomer) of 1,5-cyclooctadienerhodium(I) chloride and 5 mmol of potassium hydrotris-(3,5-dimethyl-1-pyrazolyl)borate was stirred overnight in 20 ml of DMF at room temperature. The resulting mixture was stirred with 200 ml of water and the product was extracted with methylene chloride. The extracts were chromatographed on alumina. Stripping of the eluate gave orange crystals, mp 188–190°, in 86% yield. *Anal.* Calcd for $C_{23}H_{24}BN_6Rh$: C, 54.3; H, 6.69; N, 16.5. Found: C, 54.6; H, 6.93; N, 16.5. Ir: BH at 2500 cm$^{-1}$. Nmr: s 4.20, broad peak 5.83, s 7.66, s

7.87, and broad featureless multiplet at $\tau$ 6.7–8.5 in the correct 3:4:9:9:8 ratio.

The similarly prepared $HB(3,5-(CH_3)_2pz)_3Rh(CO)_2$ had sharp singlets at $\tau$ 6.21, 7.60, and 7.66 in a 1:1:3 ratio.

**Di-$\mu$-chloro-bis($N,N$-diethylbenzylamine-*2-C,N*)dipalladium-(II).**—This material was prepared by a procedure similar to the published one[29] and was obtained after purification by chromatography in 72% yield as a yellow solid, mp 172–173°. *Anal.* Calcd for $C_{22}H_{32}Cl_2N_2Pd_2$: C, 43.5; H, 5.27; N, 4.62. Found: C, 43.5; H, 5.39; N, 4.85.

(29) A. C. Cope and E. C. Friedrich, *J. Amer. Chem. Soc.*, **90**, 909 (1968).

# Organosulfur Derivatives of the Metal Carbonyls. XIV. Reactions of Trifluoromethylthiosilver with Certain Norbornadiene- and Tetraphenylcyclobutadienemetal Complexes[1]

By R. B. King* and A. Efraty[2]

Reaction of $C_7H_8PtCl_2$ with $CF_3SAg$ in dichloromethane solution results in the replacement of both chlorine atoms with $CF_3S$ groups to give white crystalline $C_7H_8Pt(SCF_3)_2$. However, the analogous reaction of $C_7H_8PdCl_2$ with $CF_3SAg$ results in addition of $CF_3S$ groups to the norbornadiene ligand to give the two yellow crystalline products $[(C_7H_8SCF_3)Pd]_2Cl_2$ and $[(C_7H_8SCF_3)Pd]_2(Cl)(SCF_3)$ shown by their proton nmr spectra to be novel nortricyclyl derivatives. Reaction of the tetraphenylcyclobutadiene complex $[(C_6H_5)_4C_4PdBr_2]_2$ with $CF_3SAg$ in dichloromethane solution gives golden red $(C_6H_5)_4C_4Pd(SCF_3)_2$ formulated as a monomeric 16-electron tetraphenylcyclobutadiene complex. However, reaction of $(C_6H_5)_4C_4Co(CO)_2Cl$ with $CF_3SAg$ gives the dark red binuclear complex $[(C_6H_5)_4C_4Co(CO)SCF_3]_2$. The structures of these new compounds are discussed.

## Introduction

The previous paper of this series[1] reported the preparation of several trifluoromethylthio derivatives of metal carbonyls and cyclopentadienyls by reactions of the silver salt $CF_3SAg$ with various metal halide derivatives containing carbonyl and/or cyclopentadienyl groups. This paper describes the extension of $CF_3$-SAg reactions of this type to metal halides with olefinic ligands. This work resulted in the preparation of the first compounds with two terminal $CF_3S$ groups attached to a single metal atom (*i.e.*, $(C_6H_5)_4C_4Pd(SC-F_3)_2$ (I) and $C_7H_8Pt(SCF_3)_2$ (II)) as well as novel nortricyclyl derivatives of the type $[(C_7H_8SCF_3)Pd]_2XY$ (III: X = Y = Cl; X = Cl, Y = $CF_3S$) where a $CF_3S$ group had added to the organic ligand.

## Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Melting points were taken in capillaries and are uncorrected. A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions; (b) admitting to evacuated vessels. The starting materials $CF_3SAg$,[3] $C_7H_8MCl_2$ ($C_7H_8$ = norbornadiene; M = Pd,[4] Pt[5]), $[(C_6H_5)_4PdBr_2]_2$,[6] and $(C_6H_5)_4C_4Co(CO)_2Cl$[7]

(1) Part XIII: R. B. King and N. Welcman, *Inorg. Chem.*, **8**, 2540 (1969).
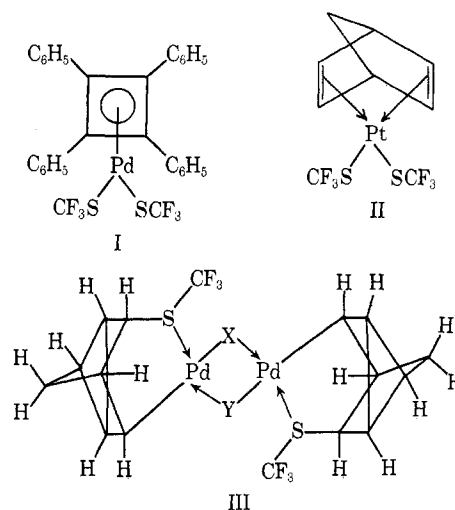
(2) Postdoctoral Research Associate, 1968–1970.

(3) H. J. Emeléus and D. E. McDuffie, *J. Chem. Soc.*, 2597 (1961).

(4) R. A. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Amer. Chem. Soc.*, **82**, 535 (1960).

(5) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1969).

(6) A. T. Blomquist and P. M. Maitlis, *J. Amer. Chem. Soc.*, **84**, 2329 (1962).

(7) A. Efraty and P. M. Maitlis, *ibid.*, **89**, 3744 (1967).



I                    II



III

were prepared according to the cited published procedures.

**Reaction of $C_7H_8PtCl_2$ with $CF_3SAg$.**—A mixture of 1.9 g (5.5 mmol) of $C_7H_8PtCl_2$, 2.3 g (11 mmol) of $CF_3SAg$, and 100 ml of dichloromethane was stirred at room temperature for 72 hr. Solvent was removed from the filtered reaction mixture at 25° (35 mm). The dry residue was crystallized from a mixture of dichloromethane and hexane to give 2.2 g (81% yield) of white $C_7H_8Pt(SCF_3)_2$. The analytical sample, mp 145–146°, was obtained by recrystallization from hot cyclohexane.

**Reaction of $C_7H_8PdCl_2$ with $CF_3SAg$.**—A mixture of 1.0 g (3.7 mmol) of $C_7H_8PdCl_2$, 1.0 g (4.8 mmol) of $CF_3SAg$, 100 ml of dichloromethane, and 40 ml of acetone was stirred for 24 hr at room temperature. Solvent was removed from the filtered reaction mixtures at ~25° (35 mm). The residue was extracted with ~250 ml of hot hexane. Upon keeping at room temperature for 2 days the filtered hexane extracts deposited 0.07 g (5.6% yield) of yellow crystalline $[(C_7H_8SCF_3)PdCl]_2$, mp 169–170°.