

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 τ 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 τ 6.21, 7.60, and 7.66 in a 1:1:3 ratio.

Di- μ -chloro-bis(*N,N*-diethylbenzylamine-2-*C,N*)dipalladium(II).—This material was prepared by a procedure similar to the published one²⁹ and was obtained after purification by chromatography in 72% yield as a yellow solid, mp 172–173°. *Anal.* Calcd for $C_{22}H_{22}Cl_2N_2Pd_2$: C, 43.5; H, 5.27; N, 4.62. Found: C, 43.5; H, 5.39; N, 4.85.

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Organosulfur Derivatives of the Metal Carbonyls. XIV. Reactions of Trifluoromethylthiosilver with Certain Norbornadiene- and Tetraphenylcyclobutadienemetal Complexes¹

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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 nortricycyl 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 series¹ 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_3S - Ag 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.*, $(C_6H_5)_4C_4Pd(SCF_3)_2$ (I) and $C_7H_8Pt(SCF_3)_2$ (II)) as well as novel nortricycyl 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 Pt⁵), $[(C_6H_5)_4C_4PdBr_2]_2$,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.

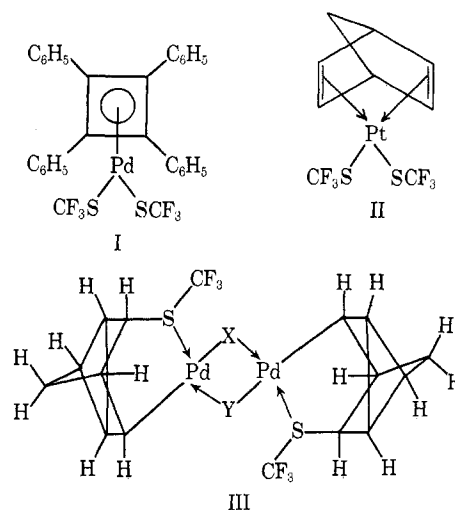
(3) H. J. Emelús and D. E. McDuffie, *J. Chem. Soc.*, 2597 (1961).

(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).

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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 $[(C_7H_8SCF_3)PdCl_2]_2$, mp 169–170°.

TABLE I
NEW TRIFLUOROMETHYLTHIO DERIVATIVES PREPARED IN THIS WORK

Compound ^a	Color	Mp, °C	Analyses, %												Mol wt ^b		¹⁹ F nmr, ϕ	Ir ν (CF) freq, cm^{-1}
			C		H		S		F		Cl		M		Calcd	Found		
$\text{C}_7\text{H}_5\text{Pt}(\text{SCF}_3)_2$	White	145-146	22.1	1.6	13.1	23.3	23.2	...	39.7	39.9	31.0	28.8	26.4 (1), 40.8 (2)	460	489	26.8	1110 s, 1098 s, 1075 s	
$[(\text{C}_7\text{H}_5\text{SCF}_3)_2\text{Pd}]_2\text{Cl}_2$	Yellow	169-170	28.7	2.4	9.5	17.0	17.1	10.6	10.3	31.7	28.9	705	42.4	670	654	42.4	1082 s, 1150 s, 1098 s	
$[(\text{C}_7\text{H}_5\text{SCF}_3)_2\text{Pd}]_2\text{ClSCF}_3$	Pale yellow	145-146	27.6	2.2	13.1	23.3	23.2	4.8	5.0	28.9	28.8	736	26.4 (1), 40.8 (2)	736	705	26.4 (1), 40.8 (2)	1185 sh, 1170 s, 1158 s, 1108 vs, 1084 sh, 1076 sh	
$(\text{C}_6\text{H}_5)_4\text{C}_4\text{Pd}(\text{SCF}_3)_2$	Red-gold	74-76	54.2	3.0	9.4	17.2	16.9	...	665	665	600	25.9	665	600	25.9	1150 s, 1130 s, 1112 sh, 1104 m, 1074 s ^e		
$[(\text{C}_6\text{H}_5)_4\text{C}_4\text{Co}(\text{CO})\text{SCF}_3]_2$	Deep red	200 dec	66.2	3.7	6.0	10.5	10.3	...	10.5	10.3	10.3	32.3	10.5	10.3	32.3	32.3	1112 sh, 1104 m, 1074 s ^e	

^a C_7H_5 = norbornadiene (bicyclo[2.2.1]heptadiene). ^b These molecular weight determinations were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., using a Mechrolab vapor pressure osmometer in CH_2Cl_2 solution. ^c These ¹⁹F nmr spectra were taken in CH_2Cl_2 solution using a Perkin-Elmer Hitachi R-20 spectrometer operating at 56.456 Mc. Chemical shifts are reported in the scale of G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959), where $\phi(\text{CFCl}_3)$ is 0.0 and $1\phi = 1$ ppm. Relative intensities are given in parentheses. ^d These infrared spectra were taken in KBr pellets and recorded on a Perkin-Elmer Model 257 spectrometer with grating optics. ^e $\nu(\text{CO})$ 2020 cm^{-1} (s).

The hexane filtrate remaining after filtering off the $[(\text{C}_7\text{H}_5\text{SCF}_3)_2\text{PdCl}]_2$ was concentrated to ~40 ml at ~25° (35 mm). The crystals which separated during this solvent removal were isolated by filtration to give 0.5 g (37% yield) of yellow $[(\text{C}_7\text{H}_5\text{SCF}_3)_2\text{Pd}]_2(\text{Cl})(\text{SCF}_3)$, mp 145-146°.

The reaction between $\text{C}_7\text{H}_5\text{PdCl}_2$ and CF_3SAg could also be carried out in dichloromethane without added acetone, but the yields of trifluoromethylthiopalladium derivatives were much lower.

Reaction of $[(\text{C}_7\text{H}_5\text{SCF}_3)_2\text{Pd}]_2(\text{Cl})(\text{SCF}_3)$ with Triphenylphosphine.—A mixture of 0.40 g (0.544 mmol) of $[(\text{C}_7\text{H}_5\text{SCF}_3)_2\text{Pd}]_2(\text{Cl})(\text{SCF}_3)$ (III: X = Cl, Y = SCF_3), 0.30 g (1.15 mmol) of triphenylphosphine, 90 ml of cyclohexane, and 10 ml of dichloromethane was stirred at room temperature. After about 12 hr a yellow precipitate started to form. After 30 hr this precipitate was filtered and dried to give 0.13 g (0.185 mmol, ~80% yield based on triphenylphosphine) of yellow $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2$, mp 283-284° (lit.⁸ mp 270° dec). *Anal.* Calcd for $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{P}_2$: C, 61.5; H, 4.3; P, 8.8; Pd, 15.1; S, 0.0; F 0.0. Found: C, 60.6; H, 4.3; P, 8.6; Pd, 14.7; S, 0.6; F, 0.8. The filtrate from the isolation of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2$ was evaporated to dryness at ~25° (40 mm). The solid residue was recrystallized from a mixture of dichloromethane and hexane to give 0.30 g (0.263 mmol, 76% yield based on triphenylphosphine) of yellow-orange $[(\text{C}_6\text{H}_5)_3\text{PPd}(\text{SCF}_3)_2]_2$, mp 205-206°. The analytical sample, mp 208-209°, was recrystallized several additional times from mixtures of dichloromethane and hexane. *Anal.* Calcd for $\text{C}_{40}\text{H}_{30}\text{F}_{12}\text{P}_2\text{Pd}_2\text{S}_4$: C, 41.9; H, 2.6; F, 20.0; P, 5.4; Pd, 18.7; S, 11.2. Found: C, 42.6; H, 2.9; F, 17.4; P, 5.1; Pd, 19.0; S, 10.7.

Reaction of $[(\text{C}_6\text{H}_5)_4\text{C}_4\text{PdBr}_2]_2$ with CF_3SAg .—A mixture of 1.0 g (0.82 mmol) of $[(\text{C}_6\text{H}_5)_4\text{C}_4\text{PdBr}_2]_2$, 0.87 g (4.16 mmol) of CF_3SAg , and 125 ml of dichloromethane was stirred for 24 hr at room temperature. Solvent was then removed from the filtered reaction mixture at ~25° (35 mm). The residue was extracted with ~150 ml of cyclohexane. Concentration of the filtered cyclohexane extracts at ~25° (35 mm) gave 0.55 g (50% yield) of reddish gold crystalline $(\text{C}_6\text{H}_5)_4\text{C}_4\text{Pd}(\text{SCF}_3)_2$, mp 74-76°.

Reaction of $(\text{C}_6\text{H}_5)_4\text{C}_4\text{Co}(\text{CO})_2\text{Cl}$ with CF_3SAg .—A mixture of 1.1 g (2.0 mmol) of $(\text{C}_6\text{H}_5)_4\text{C}_4\text{Co}(\text{CO})_2\text{Cl}$, 0.60 g (2.9 mmol) of CF_3SAg , and 150 ml of dichloromethane was stirred for 9 hr at room temperature. Solvent was removed from the filtered dichloromethane solution at ~25° (35 mm). The residue was extracted with ~200 ml of hexane to give a deep red extract. Removal of the solvent at 25° (35 mm) from the filtered hexane extract precipitated 0.22 g (20% yield) of deep red crystalline $[(\text{C}_6\text{H}_5)_4\text{C}_4\text{Co}(\text{CO})(\text{SCF}_3)]_2$, dec pt ~200°.

Proton Nmr Spectra.—The following spectra were obtained on either a Perkin-Elmer Hitachi R-20 spectrometer at 60 Mc or a Varian HA-100 spectrometer at 100 Mc using CDCl_3 solutions.

A. $\text{C}_7\text{H}_5\text{Pt}(\text{SCF}_3)_2$.—The following three resonances were observed: (1) apparent triplet at τ 4.44 (separation 2 cps) flanked by satellites arising from coupling with ¹⁹⁵Pt ($J(\text{Pt-H}) = 62$ cps) assigned to the four complexed olefinic protons of the norbornadiene ligand; (2) unresolved broad resonance at τ 5.71 (width at half-height ~12 cps) assigned to the two bridgehead protons of the norbornadiene ligand; (3) apparent singlet at τ 8.22 assigned to the two bridge protons of the norbornadiene ligand.

B. $[(\text{C}_7\text{H}_5\text{SCF}_3)_2\text{Pd}]_2\text{Cl}_2$.—Unresolved resonances were at τ 6.66, 7.18, ~8.2, and 8.48 of approximate relative intensities 1:1:4:2, respectively.

C. $[(\text{C}_7\text{H}_5\text{SCF}_3)_2\text{Pd}]_2(\text{Cl})(\text{SCF}_3)$.—Resonances were at τ 6.65 (apparent doublet, $J \approx 0.5$ cps), 7.13 (unresolved), 8.17 (complex multiplet, two apparent peaks), and 8.50 (complex multiplet, three apparent peaks) of approximate relative intensities 1:1:4:2, respectively.

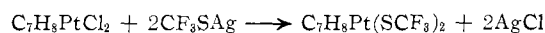
D. $(\text{C}_6\text{H}_5)_4\text{C}_4\text{Pd}(\text{SCF}_3)_2$.—Complex phenyl resonances were in two clusters centered at τ 2.5 and 2.8.

E. $[(\text{C}_6\text{H}_5)_4\text{C}_4\text{Co}(\text{CO})\text{SCF}_3]_2$.—Complex phenyl resonance (six apparent peaks) were in the range τ 2.5-2.9.

Discussion

A. **Norbornadiene Complexes.**—The white crystalline product obtained from $\text{C}_7\text{H}_5\text{PtCl}_2$ and CF_3SAg is shown to be the monomeric norbornadiene derivative $\text{C}_7\text{H}_5\text{Pt}(\text{SCF}_3)_2$ (II) on the basis of the following evidence. (1) The proton nmr spectrum exhibits the

normal 4:2:2 relative intensity pattern of resonances with chemical shifts appropriate for a complexed norbornadiene ligand.⁹ (2) The molecular weight determination in dichloromethane solution agrees with that expected for a monomer. (3) The CF₃S fluorine atoms exhibit a chemical shift of δ 26.8 in the ¹⁹F nmr spectrum which is in the rather narrow range previously¹ observed for other complexes with terminal CF₃S groups. The reaction between C₇H₈PtCl₂ and CF₃SAg can thus be formulated as a simple replacement of chlorine with CF₃S groups according to the equation



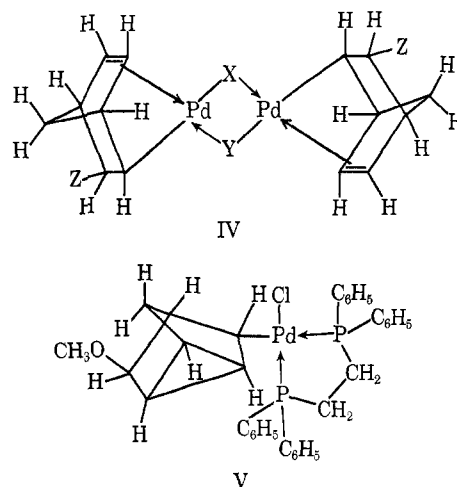
The compound C₇H₈Pt(SCF₃)₂ (II) appears to be the first reported compound with two terminal CF₃S groups attached to a single transition metal. Previous attempts¹ to prepare a titanium compound of this type, (C₅H₅)₂Ti(SCF₃)₂, led instead to formation of (C₅H₅)₂TiF₂.

One characteristic feature of the proton nmr spectra of many platinum complexes is the observation of satellites arising from coupling of the protons with the ¹⁹⁵Pt nucleus (*I* = 1/2, 34% abundance). The proton nmr spectrum of C₇H₈Pt(SCF₃)₂ (II) indicates the presence of appreciable such coupling (*J* = 62 cps) of the platinum atom with the four complexed olefinic protons but not with the remaining four protons which are more remote from the platinum atom.

The reaction between the palladium compound C₇H₈PdCl₂ and CF₃SAg gave two yellow crystalline products of stoichiometries [(C₇H₈SCF₃)Pd]₂Cl₂ and [(C₇H₈SCF₃)Pd]₂(Cl)(SCF₃). Neither of these two palladium complexes exhibits in its proton nmr spectrum the 4:2:2 relative intensity pattern and chemical shifts expected for a norbornadiene complex. Instead both palladium complexes exhibit in their proton nmr spectra a 1:1:4:2 relative intensity pattern with no protons in the usual chemical shift region for olefinic protons. The palladium complexes [(C₇H₈SCF₃)Pd]₂XY (X = Y = Cl; X = Cl, Y = SCF₃) are therefore formulated as the nortricycyl derivatives III rather than the trifluoromethylthionorbornenyl derivatives IV (Z = SCF₃) for the following reasons. (1) All protons in the nmr spectra of the [(C₇H₈SCF₃)Pd]₂XY derivatives have chemical shifts above τ 6.6 whereas the complexed olefinic protons in the known¹⁰ alkoxy-norbornenylpalladium complex [(C₇H₈OR)PdCl]₂ (IV: X = Y = Cl, Z = OR, R = CH₃, C₂H₅, etc.) exhibit an nmr chemical shift of τ ~4. However, all protons of the methoxynortricycyl ligand in the derivative CH₃O-C₇H₈PdCl(Pf-Pf) (V: Pf-Pf = (C₆H₅)₂PCH₂CH₂P-(C₆H₅)₂) exhibit nmr chemical shifts above τ 5.9.¹¹ (2) The 1,5-cyclooctadienepalladium complex C₈H₁₂PdCl₂ does not react analogously with CF₃SAg. Formation of a nortricycyl type derivative such as III is only possible when the two carbon-carbon double bonds are sufficiently close in space as is the case for norbornadiene but not 1,5-cyclooctadiene.

The compounds [(C₇H₈SCF₃)Pd]₂XY (III: X = Y = Cl; X = Cl, Y = SCF₃) thus have an unusual type of CF₃S group which bridges between a carbon atom

and a palladium atom. The ¹⁹F nmr data indicate that this type of CF₃S group exhibits a higher chemical shift (δ 40-43) than either the terminal CF₃S groups or the CF₃S groups bridging pairs of metal atoms found in this or previous¹ work. The compound [(C₇H₈SCF₃)Pd]₂(Cl)(SCF₃) (III: X = Cl, Y = SCF₃) exhibits two CF₃S resonances in the ¹⁹F nmr spectrum in a 1:2 relative area ratio consistent with the proposed structure which has two CF₃S groups of one type and one CF₃S group of another type. The chemical shift of the unique CF₃S group in [(C₇H₈SCF₃)Pd]₂(Cl)(SCF₃) (III: X = Cl, Y = SCF₃) falls in the relatively narrow range around δ 26 associated with terminal CF₃S groups bonded to transition metals; however, possible structures of this compound with one terminal CF₃S



group would have unlikely features such as three- or five-coordinate palladium (the latter is unprecedented for a yellow complex), a bridging C₇H₈SCF₃ ligand, and/or three bridging groups (unlikely for a square-planar palladium(II) complex). On the basis of presently available information we prefer formulation of [(C₇H₈SCF₃)Pd]₂(Cl)(SCF₃) with a bridging rather than terminal unique CF₃S group. The chemical shift of the unique CF₃S group can be rationalized on the basis of the wide range of chemical shifts found in only a limited number of known complexes with bridging CF₃S groups.¹

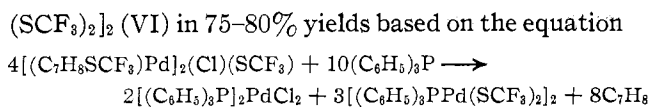
The reaction of C₇H₈PdCl₂ with CF₃SAg to form the nortricycyl derivatives III thus results in the ultimate rupture of the bonding between each metal atom and all but one carbon atom of each C₇H₈ moiety. The tendency for palladium, but not platinum, to undergo this anomalous reaction may be a consequence of the weakness of palladium-olefin bonds relative to analogous platinum-olefin bonds. In the case of the reaction of the platinum derivative C₇H₈PtCl₂ with CF₃SAg, the stability of the platinum-norbornadiene bond is sufficiently high that it remains intact under the conditions of replacement of both chlorine atoms with CF₃S groups.

In an attempt to secure additional evidence concerning the proposed structure III (X = Cl, Y = SCF₃) for [(C₇H₈SCF₃)Pd]₂(Cl)(SCF₃), its reaction with triphenylphosphine was investigated. This reaction when carried out at room temperature in a mixture of dichloromethane and cyclohexane gave the known⁸ compound [(C₆H₅)₃P]₂PdCl₂ and the new compound [(C₆H₅)₃PPd-

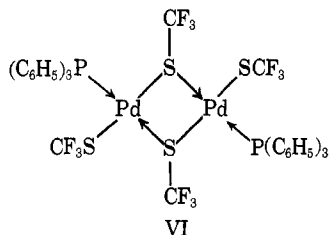
(9) M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961).

(10) J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, **88**, 5135 (1966).

(11) D. R. Coulson, *ibid.*, **91**, 200 (1969).



The triphenylphosphine thus breaks the carbon-sulfur bond in each trifluoromethylthionortricyclyl ligand as well as the palladium-carbon bond to this ligand eliminating a C_7H_5 moiety and leaving all of the trifluoromethylthio groups bonded to palladium atoms.

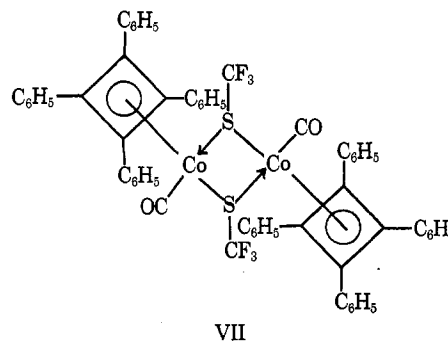


B. Tetraphenylcyclobutadiene Complexes.—The reaction between $[(\text{C}_6\text{H}_5)_4\text{C}_4\text{PdBr}_2]_2$ and CF_3SAg proceeds in a normal manner with the replacement of both halogen atoms by CF_3S groups as in the reaction between $\text{C}_7\text{H}_5\text{PtCl}_2$ and CF_3SAg discussed above. Unlike the dimeric cyclobutadienemetal dihalides of the type $[\text{R}_4\text{C}_4\text{MX}_2]_2$ ($\text{M} = \text{Ni}, \text{Pd}; \text{R} = \text{CH}_3, \text{C}_6\text{H}_5; \text{X} = \text{Cl}, \text{Br}; \text{etc.}$)¹² the palladium compound $(\text{C}_6\text{H}_5)_4\text{C}_4\text{Pd}(\text{SCF}_3)_2$ (I) is monomeric as indicated by the molecular weight determination in dichloromethane solution. The ^{19}F nmr chemical shift of the CF_3S group in $(\text{C}_6\text{H}_5)_4\text{C}_4\text{Pd}(\text{SCF}_3)_2$ (I) lies in the δ 26 region characteristic of terminal CF_3S groups (although the above data on $[(\text{C}_7\text{H}_5\text{SCF}_3)\text{Pd}]_2(\text{Cl})(\text{SCF}_3)$ suggest that this criterion must be applied with caution and is of more value in excluding the presence of terminal CF_3S groups rather than demonstrating the presence of terminal CF_3S groups). The palladium complex $(\text{C}_6\text{H}_5)_4\text{C}_4\text{Pd}(\text{SCF}_3)_2$ (I) thus appears to be the first example of a cyclobut.

(12) J. D. Dunitz, M. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 647 (1962).

adiene metal complex with a 16-electron configuration rather than the favored 18-electron configuration.¹³

The cobalt derivatives $\text{R}_4\text{C}_4\text{Co}(\text{CO})_2\text{X}$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5; \text{X} = \text{Cl}, \text{Br}, \text{I}$) are isoelectronic with the well-known cyclopentadienyliron derivatives $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ and, like the iron derivatives, are useful intermediates for the preparation of a variety of interesting organometallic derivatives.⁷ Reaction of $(\text{C}_6\text{H}_5)_4\text{C}_4\text{Co}(\text{CO})_2\text{Cl}$ with CF_3SAg results in the loss of carbon monoxide to give a deep red bimetallic derivative $[(\text{C}_6\text{H}_5)_4\text{C}_4\text{Co}(\text{CO})\text{SCF}_3]_2$ (VII). The ^{19}F nmr chemical shift of the CF_3S group is δ 32.3 which is outside the region observed for terminal CF_3S groups. The formation of a bimetallic derivative VII with bridging CF_3S groups in the reaction of CF_3SAg with $(\text{C}_6\text{H}_5)_4\text{C}_4\text{Co}(\text{CO})_2\text{Cl}$ contrasts with the formation¹ of a monometallic derivative $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SCF}_3$ in the reaction of CF_3SAg with $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ but is an obvious consequence of the weaker metal-carbon monoxide bond in the $(\text{C}_6\text{H}_5)_4\text{C}_4\text{Co}(\text{CO})_2\text{X}$ halides than in the $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ halides.⁸



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The Synthesis and Properties of Diethylenetriamine Chelates of the Tripositive Lanthanide Ions

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The reaction of diethylenetriamine with a lanthanide(III) nitrate salt in anhydrous acetonitrile yields solid compounds of the stoichiometric formulation $[\text{Ln}(\text{dien})_3](\text{NO}_3)_3$ and $[\text{Ln}(\text{dien})_2(\text{NO}_3)_2]\text{NO}_3$. Infrared data establish coordination by nitrate ion in the bis chelates. Conductivity and enthalpy data show that the $\text{Ln}(\text{dien})_2(\text{NO}_3)_2^+$ ion is the thermodynamically favored species in acetonitrile. The enthalpy changes observed for a calorimetric titration of lanthanide(III) perchlorate salts in acetonitrile demonstrate the thermodynamic stability of the $\text{Ln}(\text{dien})_n^{3+}$ ($n = 1-3$) species in solution. The variation in enthalpy changes in the lanthanide series are discussed.

Although coordination chemistry of the trivalent lanthanide ions has expanded rapidly in the last 20 years,^{1,2} the majority of complexes studied were in

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aqueous solution and were derived from anionic ligands with oxygen donor atoms. The observation that cationic complexes derived from neutral ligands with nitrogen donor sites could not be isolated from aqueous media prompted the assumption that $\text{Ln}^{3+}-\text{N}$ interactions were necessarily weaker than $\text{Ln}^{3+}-\text{O}$ interactions. Recently, however, the use of nonaqueous