

Protonation of Phosphine Complexes of Zerovalent Nickel, Palladium, Platinum, and Ruthenium with Fluorocarbon Acids

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Protonation of phosphine complexes of zerovalent nickel, palladium, and platinum with $\text{H}_2\text{C}(\text{SO}_2\text{CF}_3)_2$ yields the $\text{HC}(\text{SO}_2\text{CF}_3)_2^-$ salts of L_3MH^+ ($\text{L} = \text{Ph}_3\text{P}, \text{Ph}_2\text{PMe}, \text{Et}_3\text{P}; \text{M} = \text{Ni}, \text{Pd}, \text{Pt}$). The cations in $[(\text{Ph}_3\text{P})_3\text{PdH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$, $[(\text{Ph}_2\text{PMe})_3\text{PdH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$, $[(\text{Ph}_3\text{P})_3\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$, and $[(\text{Et}_3\text{P})_3\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ are stereochemically nonrigid in CH_2Cl_2 solution, and thermodynamic parameters for the permutational processes are reported. Protonation of $(\text{Ph}_3\text{P})_3\text{Pd}(\text{CO})$ affords fluxional $[(\text{Ph}_3\text{P})_4\text{Pd}_2(\mu-\text{CO})(\mu-\text{H})][\text{HC}(\text{SO}_2\text{CF}_3)_2]$. Protonation of $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_3$ yields $[(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_3\text{H}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$; crystal data: triclinic, $P\bar{1}$; $a = 13.261(2)$, $b = 14.216(3)$, $c = 12.912(3)$ Å; $\alpha = 96.92(3)$, $\beta = 106.72(3)$, $\gamma = 67.24(1)^\circ$; $Z = 2$.

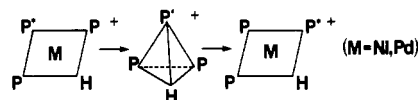
Introduction

In a series of previous papers,¹ we have reported the reactions of bis((perfluoroalkyl)sulfonyl)alkanes, exemplified by $\text{H}_2\text{C}(\text{SO}_2\text{CF}_3)_2$ (**1**), with a wide variety of transition-metal compounds containing, in addition to tertiary phosphines (usually Ph_3P), hydrides, hydrido carbonyls, hydrido carboxylates, and olefins in the ligand sets. Practical syntheses of strong fluorocarbon acids of the type $\text{HRC}(\text{SO}_2\text{R}_f)_2$ ($\text{R}_f = \text{perfluoroalkyl}$) were developed by Koshar and Mitsch.² Such acids exhibit a constellation of properties that indicate a wide potential utility in inorganic and organometallic chemistry, and they have recently been utilized to prepare novel $\eta^2\text{-H}_2$ complexes.^{3–5} Among these properties are ease of handling, with no tendency to absorb atmospheric moisture, solubility in nondonor solvents such as toluene and dichloromethane, extremely weak oxidizing strength, and a tendency not to coordinate to metal ions. Derivatives of long-chain perfluoroalkyl analogues, e.g. $\text{HC}(\text{SO}_2\text{C}_8\text{F}_{17})_2^-$, have high solubility in aromatic hydrocarbons.⁶ Their conjugate bases are not, however, the ephemeral noncoordinating anions, for bonding through the methine carbon atom [to $\text{Pt}(\text{II})$]^{1d,g} and through the sulfone oxygen atoms [to $\text{Ti}(\text{IV})$] is known.⁷ As an extension of our earlier work, we report here the reactions of **1** with a series of zerovalent phosphine-containing complexes of Ni, Pd, Pt, and Ru as well as the dynamic properties of a series of compounds of the type $[\text{L}_3\text{M}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$.

Results

The general synthetic method used here is to combine $\text{H}_2\text{C}(\text{SO}_2\text{CF}_3)_2$ and the transition-metal compound in toluene. The proton-transfer reactions proceed cleanly at room temperature and, in preparative scale reactions, appear to be complete within 1 h although longer reaction times may be used. The saltlike products, which contain $\text{HC}(\text{SO}_2\text{CF}_3)_2^-$, separate from the reaction mixture, usually in analytically pure form so that recrystallization

Scheme I



is unnecessary (although it can be accomplished by using CH_2Cl_2 -toluene). Their properties, particularly ligand permutation processes in fluid solution, are described below.

Discussion

Protonation of Nickel, Palladium, and Platinum Complexes. Reaction of $(\text{Ph}_3\text{P})_3\text{Pt}$ or $(\text{Ph}_3\text{P})_4\text{Pt}$ with 1 equiv of $\text{H}_2\text{C}(\text{SO}_2\text{CF}_3)_2$ in toluene produces $[(\text{Ph}_3\text{P})_3\text{PtH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (**2**). The $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum of **2** in dichloromethane at 9.4 T demonstrates an A_2BX pattern ($\text{A}, \text{B} = ^{31}\text{P}, \text{X} = ^1\text{H}$) with $\delta_{\text{P}} = 20.1$, $\delta_{\text{H}} = 20.3$, and $J_{\text{AX}} = -11.7$, $J_{\text{BX}} = 149$, and $J_{\text{AB}} = 18.6$ Hz. Satellites associated with the ^{195}Pt isotopomer reveal that $J_{\text{P,Pt}} = 2815$ and $J_{\text{P,H}} = 2226$ Hz. The absolute signs of $J_{\text{P,H}}$ cannot be unambiguously determined but are constrained to be of opposite sign; $J_{\text{P,Pt}}$ is taken to be positive.⁸ The Pt–P coupling constants are typical of those seen in Pt(II) complexes, and so **2** may be regarded as a cationic Pt(II) complex in distinction to protonated Pt(0). The NMR properties of **2** are very similar to those of $[(\text{Ph}_3\text{P})_3\text{PtH}][\text{BPh}_4]^{9–12}$ and indicate that platinum has the usual square-planar coordination geometry. The $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum of **2** in $\text{C}_6\text{D}_5\text{Cl}$ shows no evidence of a dynamic process up to 120 °C, indicating a high barrier to rearrangement. Like other $\text{HC}(\text{SO}_2\text{CF}_3)_2^-$ salts here reported, the ^1H and ^{19}F NMR spectra show singlets at 3.92 and -81.3 ppm, respectively, due to the fluorocarbon anion.

The reaction of $(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2\text{Pt}$ was examined to ascertain the effect of a chelating, nondissociating phosphine ligand. This change has a significant effect on the chemistry, and instead of the anticipated $[(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2\text{PtH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$, $[(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2\text{Pt}][\text{HC}(\text{SO}_2\text{CF}_3)_2]_2$ (**3**), $\delta_{31\text{P}} 48.9$ and $\delta_{19\text{F}} -81.3$, was obtained. Thus, $(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2\text{Pt}$ acts as a reducing agent toward **1**. This is only the second example of such an electron-transfer process involving $\text{H}_2\text{C}(\text{SO}_2\text{CF}_3)_2$, the other occurring with $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{CO})_2]_2$, which forms $[\text{trans}-(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})_2][\text{HC}(\text{SO}_2\text{CF}_3)_2]^{1k}$.

Zerovalent nickel and palladium complexes containing monodentate phosphines are also readily protonated by **1**, a reaction that, with HX ($\text{X} = \text{Cl}, \text{CN}$), leads to oxidation and formation of Pd(II) derivatives.⁹ In earlier work, protonation of L_4M ($\text{L} = \text{Et}_3\text{P}, \text{Me}_3\text{P}, \text{PhPMe}_2; \text{M} = \text{Pt}, \text{Pd}$) with ethanol followed by

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Table I. Analytical, Yield, and Infrared^a Data

compd	anal. calcd, % (found, %)	yield, %	ν_{MH} , cm^{-1}
$[(\text{Ph}_3\text{P})_3\text{PtH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (2)	C, 54.2 (54.1); H, 3.7 (3.8)	92	2088
$[(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2\text{Pt}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (3)	C, 44.9 (44.6); H, 3.2 (3.5)	67	
$[(\text{Ph}_2\text{PMe})_3\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (4)	C, 53.7 (54.0); H, 4.4 (4.4)	53	2042
$[(\text{Ph}_3\text{P})_3\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (5)	C, 60.8 (60.6); H, 4.2 (4.1); F, 10.1 (10.5); S, 5.7 (5.7)	87	1965
$[(\text{EtO})_3\text{P}]_4\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (6)	C, 32.3 (32.3); H, 6.2 (6.3)	71	1995
$[(\text{Ph}_2\text{PMe})_3\text{PdH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (7)	C, 51.1 (51.0); H, 4.2 (4.1)	62	1909
$[(\text{Ph}_3\text{P})_3\text{PdH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (8)	C, 58.5 (58.0); H, 4.0 (3.8); F, 9.7 (10.3); S, 5.5 (5.8)	69	1986
$[(\text{Et}_3\text{P})_3\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (9)	C, 36.4 (36.8); H, 6.8 (6.8)		
$[(\text{Ph}_3\text{P})_4\text{Pd}_2(\text{CO})\text{H}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (10)	C, 58.2 (58.4); H, 4.0 (3.9); P, 7.9 (7.8); Pd, 13.5 (13.8); S, 4.1 (4.0)	76	
$[(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})\text{H}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (11)	C, 51.0 (50.8); H, 3.2 (3.3)	61	1943 ^b

^aNujol mulls, $\pm 3 \text{ cm}^{-1}$. ^bFrom Raman spectrum.

Table II. NMR Data

compd	¹ H, ³¹ P chem shifts (no., coupling consts) ^a
2	¹ H, -5.74 (dt); ³¹ P, 20.1 (2 P, $J_{\text{P-Pt}} = 2815$, $J_{\text{P-P}} = 19$, $J_{\text{P-H}} = \pm 12$), 20.3 (1 P, $J_{\text{P-Pt}} = 2226$, $J_{\text{P-H}} = \pm 149$)
3	³¹ P, 48.9 ($J_{\text{P-Pt}} = 2309$)
4	¹ H, -17.5; ³¹ P, 1.1 (br s at -90 °C) ^b
5	¹ H, -12.8; ³¹ P, 25.0 (2 P, $J_{\text{P-H}} = 60$, $J_{\text{P-P}} = 20$), 24.2 (1 P, $J_{\text{P-H}} = 88$) ^c
6	¹ H, -14.5 (quintet, $J_{\text{P-H}} = 26$); ³¹ P, 134.2 (at -90 °C) ^b
7	¹ H, -6.65 ($J_{\text{P-H(trans)}} = 191$), 1.13 (6 H, CH_3), 1.62 (3 H, CH_3); ³¹ P, 10.9 (2 P, $J_{\text{P-P}} = 28$, $J_{\text{P-H}} = 28$), 1.6 (1 P, $J_{\text{P-H}} = 8$)
8	¹ H, -6.95; ³¹ P, 29.0 (2 P, $J_{\text{P-P}} = 29$), 21.0 (1 P)
9	¹ H, -18.9 (dt, $J_{\text{P-H(cis)}} = 67$, $J_{\text{P-H(trans)}} = 96$); ³¹ P, 17.4 (2 P, $J_{\text{P-P}} = 21$), 15.8 (1 P)

^aIn CD_2Cl_2 . Chemical shifts in ppm relative to internal $(\text{CH}_3)_4\text{Si}$ or external H_3PO_4 with downfield shifts being positive; coupling constants in Hz. ^bInvariant to -90 °C. ^cAt -65 °C.

addition of $\text{Na}[\text{BPh}_4]$ produced $[\text{L}_3\text{MH}][\text{BPh}_4]$.¹³ One Ph_3P ligand is lost from L_4M ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) upon proton transfer, but in $[(\text{EtO})_3\text{P}]_4\text{Ni}$, all of the phosphite ligands are retained.¹⁴⁻²⁰ Thus, addition of 1 equiv of $\text{H}_2\text{C}(\text{SO}_2\text{CF}_3)_2$ to L_4Ni or L_4Pd in toluene leads to precipitation of the crystalline salts $[(\text{Ph}_2\text{PMe})_3\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (4), $[(\text{Ph}_3\text{P})_3\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (5), $[(\text{EtO})_3\text{P}]_4\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (6), $[(\text{Ph}_2\text{PMe})_3\text{PdH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (7), and $[(\text{Ph}_3\text{P})_3\text{PdH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (8). The compound $[(\text{Et}_3\text{P})_3\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (9) was obtained as an oil that could not be induced to crystallize. Yields and infrared and analytical data are given in Table I, and NMR data, in Table II. These $[\text{L}_3\text{MH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ materials are air-sensitive orange ($\text{M} = \text{Ni}$) or yellow ($\text{M} = \text{Pd}$) microcrystalline solids that are stable indefinitely under nitrogen. In particular, 6 has remained unchanged as a free-flowing solid after 2.5 years in a drybox whereas $[(\text{EtO})_3\text{P}]_4\text{NiH}][\text{HSO}_4]$ decomposes on standing.¹⁷ No reaction was observed between 1 and $[(\text{PhO})_3\text{P}]_4\text{Ni}$, $[\text{CpNi}(\text{CO})_2]_2$, or $(\text{Ph}_3\text{P})_2\text{Ni}(\text{CO})_2$, possibly because the metal center is less electron-rich in these compounds.

Ligand association and intramolecular rearrangements in $[\text{L}_3\text{MH}][\text{BPh}_4]$ compounds have previously been studied by DNMR spectroscopy.^{14,15} Stereochemical nonrigidity of $[\text{L}_3\text{MH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ compounds in dichloromethane solution has been studied by variable-temperature $\{^1\text{H}\}^{31}\text{P}$ NMR spectroscopy. At low temperatures, 7-9 have static structures in which the metal has essentially a square-planar coordination geometry with two phosphine ligands cis to the hydride ligand and one trans to it. At 4.7 T, the chemical shift difference between these two types of phosphorus nuclei is sufficiently large to yield unambiguous A_2X spectra. A rearrangement process such as that shown

Table III. Barriers to Rearrangement in L_3MH^+ Derivatives^a

compd	ΔH^\ddagger	ΔS^\ddagger	ΔG^\ddagger at 0 °C
$[(\text{Ph}_3\text{P})_3\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$	5.7 ± 0.8	-25 ± 4	12.43
$[(\text{Ph}_2\text{PMe})_3\text{PdH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$	2.9 ± 0.2	-32 ± 2	12.23
$[(\text{Ph}_3\text{P})_3\text{PdH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$	6.6 ± 0.3	-27 ± 3	13.98
$[(\text{Et}_3\text{P})_3\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$	5.5 ± 0.4	-29 ± 4	13.40

^aFree energies and enthalpies in kcal mol^{-1} ; entropies in eu.

in Scheme I permutes the ³¹P environments and leads to an A_3 spectral pattern. This scheme invokes an equilibrium between square-planar ground-state coordination geometry and an intermediate or transition state in which the metal has become tetrahedral. Planar Ni(II) has $S = 0$ but $S = 1$ for the tetrahedral isomer, and therefore, such equilibria have been directly detected by isotropically shifted NMR spectra in $(\text{phosphine})_2\text{Ni}(\text{halide})_2$ complexes.²¹⁻²⁵

The limiting low-temperature ³¹P NMR spectrum of $[(\text{Ph}_2\text{PMe})_3\text{PdH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ in CD_2Cl_2 (at -80 °C) yields $\delta_{\text{P}_a} = 10.9$, $\delta_{\text{P}_x} = 1.6$, and $^2J_{\text{P}_a\text{P}_x} = 28$ and $^2J_{\text{P}_a\text{H}} = 190$ Hz. Computer simulation of the spectra (cf. Experimental Section) yields $\Delta H^\ddagger = 2.9 \pm 0.2 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -32 \pm 2 \text{ eu}$ for the rearrangement process. Retention of $\text{P}_a\text{-P}_x$ coupling indicates that the reaction is intramolecular. Addition of 1 equiv of $[n\text{-Pr}_4\text{N}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ changes ΔH^\ddagger to $3.9 \pm 0.2 \text{ kcal mol}^{-1}$; ΔS^\ddagger ($32 \pm 2 \text{ eu}$) is unchanged. We regard this perturbation as being so small as to indicate that ligand permutation in 7 does not occur via a five-coordinate intermediate in which the $\text{HC}(\text{SO}_2\text{CF}_3)_2^-$ anion is covalently bonded to palladium.

Rearrangements in $[(\text{Ph}_3\text{P})_3\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ are more complicated. The ³¹P NMR spectrum at ≤ -65 °C demonstrates an A_2BX pattern (although resolution is suboptimal, probably because of paramagnetic impurities in this exceedingly oxygen-sensitive compound). At 5 °C, the ³¹P spectral lines coalesce to a singlet having a line width of 56 Hz and analysis of the intervening DNMR spectra gives $\Delta H^\ddagger = 5.7 \pm 0.8 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -25 \pm 4 \text{ eu}$ for the ligand permutation reaction. However, an additional reversible line-broadening process occurs: at +9 °C, the ³¹P line width increases to 70 Hz and increases to 110 Hz at 22 °C. We surmise that this higher temperature line broadening is due to thermally activated population of the tetrahedral, paramagnetic $S = 1$ state.²¹

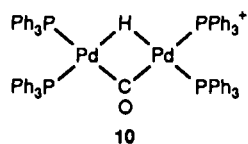
DNMR data for $[\text{L}_3\text{MH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ compounds, collected in Table III, reveal some interesting trends. The barrier to rearrangement is in the order $\text{Pt} \gg \text{Pd} > \text{Ni}$, and thus, the $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum of $[(\text{Ph}_2\text{PMe})_3\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$, the nickel

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analogue of **7**, remains a broad singlet down to $-90\text{ }^\circ\text{C}$. The limited data set suggests that making the phosphine ligand more basic, or increasing its cone angle, increases the barrier to rearrangement. The enthalpy of activation for rearrangement of $[(\text{Et}_3\text{P})_3\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ in CD_2Cl_2 , $5.5 \pm 0.4\text{ kcal mol}^{-1}$, is significantly lower than that reported for intramolecular ligand exchange in $[(\text{Et}_3\text{P})_3\text{NiH}][\text{BPh}_4^-]$ in acetone, 9.6 kcal mol^{-1} , and the entropy of activation, -29 ± 4 versus -7.9 eu, much higher. The combined effect of these differences is to make ΔG^\ddagger (scaled to $-73\text{ }^\circ\text{C}$) for the $\text{HC}(\text{SO}_2\text{CF}_3)_2^-$ salt of $(\text{Et}_3\text{P})_3\text{NiH}^+$ 1.3 kcal mol^{-1} lower than for the BPh_4^- salt.

Protonation of $(\text{Ph}_3\text{P})_4\text{Pd}$ in toluene, under an atmosphere of carbon monoxide, with $\text{H}_2\text{C}(\text{SO}_2\text{CF}_3)_2$ affords binuclear $[(\text{Ph}_3\text{P})_4\text{Pd}_2(\mu\text{-CO})(\mu\text{-H})][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ [**10**; ν_{CO} 1851 cm^{-1} (Nujol)]. Equivalent results are obtained by starting with pre-



formed $(\text{Ph}_3\text{P})_3\text{Pd}(\text{CO})$ and using a CO atmosphere, but when an argon atmosphere is employed, **8** is produced. The structure of **10** is quite probably similar to that of the crystallographically characterized platinum compound $[(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2\text{Pt}_2(\mu\text{-CO})(\mu\text{-H})][\text{BF}_4^-]$, for which, in the $\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$ derivative, $J_{\text{P-H}(\text{trans})} = 78$ and $J_{\text{P-H}(\text{cis})} = 15\text{ Hz}$ (vide infra).²⁷ Like this congener, **10** is stereochemically nonrigid. This is apparent from the ^{13}C NMR spectra of the ^{13}C -labeled derivative. At $-30\text{ }^\circ\text{C}$, the carbonyl carbon gives rise to a binomial quintet centered at 227.2 ppm , having $J_{\text{PC}} = 33\text{ Hz}$. Upon cooling, both peaks broaden and then, at $-110\text{ }^\circ\text{C}$, give rise to a 73-Hz triplet, only $J_{\text{P-C}(\text{trans})}$ being observable. The variable-temperature ^{31}P NMR spectra show analogous behavior. At $-30\text{ }^\circ\text{C}$, a 33-Hz doublet at 23.2 ppm is observed. The limiting low-temperature spectrum, obtained at $-110\text{ }^\circ\text{C}$, comprises a doublet, $J_{\text{PP}} = 37\text{ Hz}$, at 28.0 ppm and a doublet, $J_{\text{PP}} = 39$ and $J_{\text{PC}} = 73\text{ Hz}$, at 18.3 ppm . The dynamic process is also manifest in the ^1H spectra. The hydride region at $-60\text{ }^\circ\text{C}$ contains a binomial 40-Hz quintet at -6.06 ppm that transforms at $-110\text{ }^\circ\text{C}$ to a triplet of triplets, $J_{\text{P-H}(\text{trans})} = 93$ and $J_{\text{P-H}(\text{cis})} = \text{ca. } -12\text{ Hz}$. The barrier to rearrangement in **10** was determined by ^{31}P DNMR spectra of the ^{12}C compound (cf. Experimental Section) between -108 and $-50\text{ }^\circ\text{C}$, which demonstrate the typical conversion of an AX spin system into an A_2 singlet as the temperature is raised. A least-squares fit of ΔG^\ddagger versus temperature ($8.14\text{ kcal mol}^{-1}$ at $-110\text{ }^\circ\text{C}$ to $7.80\text{ kcal mol}^{-1}$ at $-60\text{ }^\circ\text{C}$) yields $\Delta H^\ddagger = 9.5 \pm 0.4\text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 8 \pm 4\text{ eu}$.

The process that permutes chemically nonequivalent ^{31}P environments is viewed as involving cleavage of either a Pd-H or a Pd-C bridge bond followed by rotation about the remaining Pd-X-Pd bond. The positive entropy of activation is consistent with such a picture. Because the process is intramolecular, a distinction between the two possibilities cannot be made from any DNMR studies. Re-formation of the dimer structure in **10** has a 50:50 probability of exchanging a given Ph_3P ligand on one side of the cation with respect to the CO or hydride ligands. In this case, the actual rate of Pd-H (or Pd-C) bond breaking is 4-fold faster than that measured by the rate of interconversion of ^{31}P environments and, concomitantly, ΔS^\ddagger would increase by 2.7 eu. The limiting low-temperature ^1H NMR spectrum of $[(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2\text{Pt}_2(\mu\text{-CO})(\mu\text{-H})][\text{BF}_4^-]$ was observed at $-62\text{ }^\circ\text{C}$ (at 80 MHz) whereas a temperature of $-110\text{ }^\circ\text{C}$ is necessary to achieve a comparable proton spectrum of **10** at 200 MHz . On the basis of the observed ^{31}P chemical shifts (10.6 and 21.5 ppm at 32.4 MHz), the free energy of activation for ^{31}P permutation in this platinum cation is at least $10.5\text{ kcal mol}^{-1}$.

Protonation of Fe(0) and Ru(0) Complexes. Structure of $[(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_3\text{H}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$. Empirically, carbonyl com-

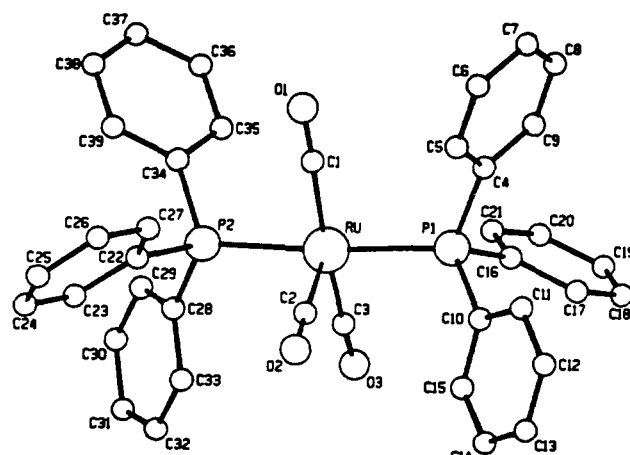


Figure 1. PLUTO drawing of the $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_3\text{H}^+$ cation in **11**.

Table IV. Bond Distances and Angles in the $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_3\text{H}^+$ Cation in **11**

Distances (\AA)			
Ru-P1	2.395 (1)	Ru-C3	1.949 (6)
Ru-P2	2.394 (1)	C1-O1	1.122 (6)
Ru-C1	1.942 (6)	C2-O2	1.101 (6)
Ru-C2	2.007 (6)	C3-O3	1.126 (6)
Angles (deg)			
P1-Ru-P2	173.66 (5)	C2-Ru-C3	97.7 (2)
P1-Ru-C3	88.3 (1)	C1-Ru-C2	96.8 (2)
P2-Ru-C2	94.1 (2)	Ru-C1-O1	175.1 (5)
P2-Ru-C1	87.3 (1)	Ru-C2-O2	177.6 (5)
P1-Ru-C1	91.9 (1)	Ru-C3-O3	176.9 (5)
P1-Ru-C2	92.3 (2)		

plexes of iron and ruthenium appear to be much less basic than those of palladium and platinum. Thus, we observe no new, isolable products when $(\text{Ph}_3\text{P})\text{Fe}(\text{CO})_4$, $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$, $(\text{Ph}_3\text{P})\text{Ru}_3(\text{CO})_{11}$, or $(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)\text{Ru}_3(\text{CO})_{10}$ is treated with **1** in toluene. The complex $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_3$, however, is protonated under these conditions to produce $[(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_3\text{H}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (**11**). In CH_2Cl_2 solution, **11** displays ν_{CO} bands at 2072 (s) and 2052 (s) cm^{-1} . An additional band, attributable to Ru-H stretching, is not apparent but the Raman spectrum of the solid displays a scattering peak at 1943 cm^{-1} for which this assignment is plausible. The data are in agreement with those for $[(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_3\text{H}][\text{PF}_6^-]$.²⁸ The gross molecular architecture is established by the uncoupled ^{31}P NMR spectrum, which comprises a 15-Hz doublet at 34.5 ppm , and by the ^1H NMR spectrum, in which the Ru-H proton appears as a triplet at -6.2 ppm with $J_{\text{PH}} = 15\text{ Hz}$.

The structure of the $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_3\text{H}^+$ cation in **11** is shown in Figure 1, and selected bond distances and angles are given in Table IV. The coordination geometry about ruthenium is approximately octahedral. The two Ph_3P ligands occupy trans positions, with the P1-Ru-P2 angle being $173.66(5)^\circ$; the two Ru-P bond lengths are experimentally equivalent. The C2-Ru-C3, P2-Ru-C2, and P2-Ru-C1 angles are $97.7(2)$, $94.1(2)$, and $87.3(1)^\circ$, respectively. The hydrogen atom bonded to ruthenium was not located in the electron density difference maps, but owing to its structural trans effect, its position antipodal to C2-O2 is apparent. Thus, $d(\text{Ru-C2})$, $2.007(6)\text{ \AA}$, is significantly longer than $d(\text{Ru-C1})$ and $d(\text{Ru-C3})$, which are $1.942(6)$ and $1.949(6)\text{ \AA}$, respectively. Likewise, the C2-O2 bond, $1.101(6)\text{ \AA}$, is contracted relative to $d(\text{C1-O1})$ and C3-O3 , $1.122(6)$ and $1.126(6)\text{ \AA}$, respectively. Interatomic distances and angles of the $\text{HC}(\text{SO}_2\text{CF}_3)_2^-$ anion, available as supplementary material, are

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Table V. Crystallographic Data for $[(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_3\text{H}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$

chem formula	fw 989.86
$\text{C}_{42}\text{H}_{32}\text{F}_6\text{RuO}_7\text{P}_2\text{S}_2$	space group $P\bar{1}$
$a = 13.261(2) \text{ \AA}$	$T = 23 \text{ }^\circ\text{C}$
$b = 14.216(3) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$c = 12.912(3) \text{ \AA}$	$\rho_{\text{calcd}} = 1.53 \text{ g cm}^{-3}$
$\alpha = 96.92(3)^\circ$	$\mu = 6.0 \text{ cm}^{-1}$
$\beta = 106.72(3)^\circ$	max, min, av transm
$\gamma = 77.24(1)^\circ$	factors 0.999, 0.946, 0.967
$V = 2149.7 \text{ \AA}^3$	$R = 0.042$
$Z = 2$	$R_w = 0.045$

essentially the same as found previously in salts containing organometallic cations.^{3,4,6,7}

Experimental Section

Reactions were carried out, unless otherwise specified, under a water- and oxygen-free nitrogen atmosphere. Toluene was distilled from Na-K alloy. NMR samples were prepared on a vacuum line by using CD_2Cl_2 distilled from CaH_2 . Infrared spectra were obtained on mulls prepared in a drybox from Nujol that had been boiled with sodium. NMR spectra were obtained on Varian XL-200 and 400 spectrometers operating at 200 and 400 MHz (^1H), respectively. ^{31}P spectra were obtained both with and without ^1H decoupling. Positive chemical shifts are downfield of internal $(\text{CH}_3)_4\text{Si}$ or CFCl_3 or external 85% H_3PO_4 . Dynamic NMR spectra were calculated on a DEC VAX 11/780 computer with use of DYNAMAR, a program for evaluation of intramolecular exchange that was originally written by P. Z. Meakin, as previously described.¹¹ The program was locally modified to automatically vary the exchange rate to fit either a line width or a valley between two peaks.¹¹ Errors in the activation parameters were determined by the method of Newmark et al.²⁹ Spectra of **2** were calculated by using the Varian iterative software, which is based on the LAOCOON 3 program. Phosphine complexes of nickel, palladium, and platinum were obtained from the Strem Chemical Co. The fluorocarbon acid $\text{H}_2\text{C}(\text{SO}_2\text{CF}_3)_2$ was prepared by the method of Koshar and Mitsch² and was provided by Robert Koshar, 3M Industrial and Electronic Sector Research Laboratory. Samples of Ni and Pd salts were loaded into NMR tubes in a drybox, and CD_2Cl_2 was added by distillation on a high-vacuum line. The Ni compounds are extremely air sensitive in solution, and to obtain reliable DNMR data, rigorous exclusion of oxygen is necessary.

$[(\text{Ph}_2\text{PMe})_2\text{NiH}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (**4**). Most of the new compounds reported here were prepared by the exemplary general method used for this nickel hydride complex. A solution of 0.28 g (1 mmol) of $\text{H}_2\text{C}(\text{SO}_2\text{CF}_3)_2$ in 2 mL of toluene was added with stirring to 0.89 g (1 mmol) of $(\text{Ph}_2\text{PMe})_2\text{Ni}$ in 15 mL of toluene. After the mixture was stirred for 2 h, the yellow crystalline product was isolated by filtration, washed with fresh solvent, and dried under vacuum. The yield was 0.5 g (53%).

$[(\text{Ph}_3\text{P})_4\text{Pd}(\mu\text{-CO})(\mu\text{-H})][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (**10**). A brisk stream of carbon monoxide was passed for 15 min through a solution of 1.0 g (0.87 mmol) of $(\text{Ph}_3\text{P})_4\text{Pd}$ in 12 mL of toluene. [Addition of CO-saturated ethanol at this point precipitates yellow, microcrystalline $(\text{Ph}_3\text{P})_3\text{Pd}(\text{CO})$, $\nu_{\text{CO}} 1955 \text{ cm}^{-1}$, 94% yield.] Next, a solution of 0.25 g (0.87 mmol) of **1** in 4 mL of toluene was added dropwise with stirring. After the mixture was stirred for 16 h under a CO atmosphere, the yellow microcrystalline product was collected on a filter, washed with fresh solvent, and vacuum-dried. The yield was 0.52 g (76%).

A solution of 0.1 g of **10** in 2 mL of CH_2Cl_2 was stirred for 48 h under a 700-mm pressure of ^{13}CO . Evaporation of the solvent yielded the ^{13}C -labeled product, $\nu_{\text{CO}} 1810 \text{ cm}^{-1}$.

$[(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_3\text{H}][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ (**11**). A mixture of 0.33 g (0.33 mmol) of $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_3$,²⁸ 0.1 g (0.36 mmol) of **1**, and 5 mL of toluene was stirred for 24 h. The solid phase was isolated by filtration in air and then chromatographed on a 8×0.5 in. silica gel column. Dichloromethane eluted a small amount of oil. **11** was eluted with 1:2 CH_2Cl_2 -acetone. Recrystallization by slow evaporation of a CH_2Cl_2 -toluene solution gave 0.2 g (61%) of white crystals, one of which was used for the structure determination. Crystallographic data was summarized in Table V. Atomic positional parameters are given in Table VI.

Crystallography. A colorless, needle-shaped crystal of **11** of approximate dimensions $0.08 \times 0.18 \times 0.32$ mm was mounted on a glass fiber so that the long crystal axis was roughly parallel to the goniometer φ axis. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 25 reflections in the range $10 < \theta < 15^\circ$ measured by the computer-controlled diagonal slit method of centering. There was no systematic absences, and the space group was determined to be $P\bar{1}$. Data were collected to $2\theta_{\text{max}}$ of 48° by using the ω - θ scan technique with a rate varying from 1 to $10^\circ \text{ min}^{-1}$ in ω . The scan rate was determined as a function of θ to correct

Table VI. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	$B_i^a \text{ \AA}^2$
Ru	0.26789 (3)	0.23269 (3)	0.24015 (4)	2.909 (9)
S1	0.7228 (1)	0.6585 (1)	0.1631 (1)	4.63 (4)
S2	0.7965 (1)	0.7969 (1)	0.3274 (1)	5.71 (5)
P1	0.1577 (1)	0.13406 (9)	0.1460 (1)	2.88 (3)
P2	0.3627 (1)	0.3395 (1)	0.3453 (1)	3.15 (3)
F1	0.6525 (4)	0.9347 (3)	0.1842 (4)	9.4 (2)
F2	0.7323 (4)	0.9949 (3)	0.3282 (5)	11.9 (2)
F3	0.6010 (3)	0.9432 (4)	0.3275 (4)	10.3 (2)
F4	0.8417 (4)	0.4825 (3)	0.0944 (4)	11.0 (2)
F5	0.9393 (3)	0.5488 (3)	0.2171 (4)	9.8 (2)
F6	0.8375 (4)	0.4819 (3)	0.2557 (4)	11.2 (2)
O1	0.1111 (3)	0.4215 (3)	0.1031 (3)	5.5 (1)
O2	0.4432 (3)	0.1359 (3)	0.1044 (4)	6.8 (1)
O3	0.3783 (3)	0.0743 (3)	0.4216 (3)	6.1 (1)
O4	0.7423 (3)	0.7063 (3)	0.0828 (3)	6.1 (1)
O5	0.6274 (3)	0.6272 (3)	0.1354 (4)	6.4 (1)
O6	0.8799 (3)	0.7902 (4)	0.2743 (4)	7.5 (1)
O7	0.8217 (5)	0.7995 (4)	0.4433 (4)	9.9 (2)
C1	0.1695 (4)	0.3501 (4)	0.1492 (4)	3.6 (1)
C2	0.3805 (4)	0.1722 (4)	0.1516 (5)	4.1 (1)
C3	0.3402 (4)	0.1308 (4)	0.3537 (4)	3.9 (1)
C4	0.0289 (4)	0.2051 (3)	0.0469 (4)	3.0 (1)
C5	0.0352 (4)	0.2508 (4)	-0.0407 (4)	3.8 (1)
C6	-0.0600 (5)	0.3063 (4)	-0.1152 (4)	4.5 (2)
C7	-0.1646 (5)	0.3178 (4)	-0.1064 (5)	4.8 (2)
C8	-0.1730 (4)	0.2737 (4)	-0.0226 (5)	4.9 (2)
C9	-0.0772 (4)	0.2177 (4)	0.0539 (4)	3.8 (1)
C10	0.2352 (4)	0.0249 (4)	0.0732 (4)	3.3 (1)
C11	0.1922 (4)	0.0035 (4)	-0.0342 (4)	4.4 (2)
C12	0.2516 (5)	-0.0822 (4)	-0.0845 (5)	5.6 (2)
C13	0.3540 (5)	-0.1469 (4)	-0.0281 (5)	6.1 (2)
C14	0.3982 (5)	-0.1285 (5)	0.0788 (6)	5.7 (2)
C15	0.3390 (4)	-0.0425 (4)	0.1278 (5)	4.4 (2)
C16	0.1082 (4)	0.0766 (4)	0.2312 (4)	3.2 (1)
C17	0.0946 (4)	-0.0165 (4)	0.2018 (4)	3.8 (1)
C18	0.0516 (4)	-0.0566 (4)	0.2634 (4)	4.5 (1)
C19	0.0210 (5)	-0.0061 (4)	0.3523 (4)	5.3 (2)
C20	0.0347 (5)	0.0837 (5)	0.3819 (5)	6.7 (2)
C21	0.0797 (5)	0.1252 (4)	0.3239 (4)	5.0 (1)
C22	0.4484 (4)	0.3727 (3)	0.2783 (4)	3.4 (1)
C23	0.5518 (5)	0.3773 (4)	0.3342 (5)	5.2 (2)
C24	0.6150 (4)	0.4042 (5)	0.2830 (5)	6.2 (2)
C25	0.5752 (5)	0.4280 (4)	0.1756 (5)	5.7 (2)
C26	0.4729 (5)	0.4259 (4)	0.1201 (5)	5.3 (2)
C27	0.4100 (4)	0.3977 (4)	0.1691 (4)	4.6 (1)
C28	0.4643 (4)	0.2857 (3)	0.4734 (4)	3.1 (1)
C29	0.4570 (4)	0.3371 (4)	0.5707 (4)	4.0 (1)
C30	0.5399 (5)	0.2958 (5)	0.6648 (5)	5.8 (2)
C31	0.6283 (5)	0.2063 (5)	0.6627 (5)	6.0 (2)
C32	0.6354 (5)	0.1547 (4)	0.5656 (6)	5.5 (2)
C33	0.5528 (4)	0.1942 (4)	0.4717 (5)	4.5 (2)
C34	0.2686 (4)	0.4618 (4)	0.3840 (4)	3.8 (1)
C35	0.1819 (5)	0.4655 (5)	0.4255 (5)	5.8 (2)
C36	0.1124 (5)	0.5583 (6)	0.4592 (6)	7.5 (2)
C37	0.1292 (6)	0.6466 (5)	0.4506 (6)	6.9 (2)
C38	0.2133 (6)	0.6430 (4)	0.4109 (5)	6.1 (2)
C39	0.2837 (5)	0.5512 (4)	0.3780 (5)	4.6 (2)
C40	0.7290 (5)	0.7173 (5)	0.2821 (5)	5.1 (2)
C41	0.6886 (5)	0.9231 (5)	0.2896 (6)	7.2 (2)
C42	0.8398 (6)	0.5369 (5)	0.1843 (6)	7.1 (2)

^a B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

for the separation of the $K\alpha$ doublet. The intensities of three check reflections, measured every 120 min, remained constant to within experimental error.

Lorentz and polarization corrections to the data were applied as was an empirical absorption correction (based on a series of ψ scans) of 6.0 cm^{-1} . Intensities of equivalent reflections were averaged with the agreement factors for 796 observed and accepted reflections being 2.2% (based on intensity) and 1.8% (based on F_o). Reflections of the class 001 (supplementary material, p S28) were inadvertently omitted from the averaging. Because of their small number (10) compared to the total

data set (4210 reflections), there should be no significant effect on the final results. The maximum discrepancy between two unaveraged measurements was 2σ , and most discrepancies were considerably less. We thank a very careful reviewer for drawing this point to our notice.

The structure was solved by using the Patterson heavy-atom method, which revealed the position of the Ru atom. Remaining atoms were located in successive difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined.

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Supplementary Material Available: Tables giving a summary of crystallographic procedures, calculated hydrogen atom positions (Table S1), bond distances and angles (Table S2), and general displacement parameters (Table S3) and figures showing atom-numbering schemes (14 pages); a listing of observed and calculated structure factors (Table S4) (43 pages). Ordering information is given on any current masthead page.

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Metallacarborane Complexes That Incorporate the Lanthanides. Synthesis, Molecular Structure, and Spectroscopic Characterization of Dicarbollide Complexes of Samarium and Ytterbium

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The interaction of $\text{Na}_2[\text{nido-7,8-C}_2\text{B}_9\text{H}_{11}]$ (**1**) with LnI_2 ($\text{Ln} = \text{Sm}, \text{Yb}$) in THF affords a complex with the composition $\text{Ln}(\text{C}_2\text{B}_9\text{H}_{11})(\text{THF})_4$ ($\text{Ln} = \text{Sm}$ (**2**), Yb (**3**)). Both these complexes have been fully characterized by spectroscopic techniques, and the molecular structure of the DMF derivative of **3** has been established by a single-crystal X-ray diffraction study. The DMF derivative, $\text{Yb}(\text{C}_2\text{B}_9\text{H}_{11})(\text{DMF})_4$ (**3b**), crystallizes in the orthorhombic space group *Pbca* with $a = 10.208$ (1) Å, $b = 17.005$ (3) Å, $c = 31.627$ (5) Å, $V = 5479$ Å³, and $Z = 8$. Data were collected on a modified Picker FACS-1 diffractometer at 25 °C using Mo K α radiation, to a maximum $2\theta = 50^\circ$, giving 4841 unique reflections, and the structure was solved by statistical methods. The final discrepancy index was $R = 0.082$, $R_w = 0.084$ for 1424 independent reflections with $I > 2\sigma(I)$. The dicarbollide ligand is η^2 -bound to the Yb ion, and four DMF molecules are coordinated to Yb through the oxygen atoms. Complex **2** is fluxional in solution. The fluxionality of complex **2** in solution has been monitored by variable-temperature ¹¹B NMR spectroscopy, and a dynamic process involving the Sm^{2+} ion and the dicarbollide ligand has been proposed. The reaction of *closo*-1,1,1,1-(THF)₄-1,2,3-LnC₂B₉H₁₁ ($\text{Ln} = \text{Sm}$ (**2**), Yb (**3**)) with $[\text{PPN}]^+[\text{closo-3,1,2-TiC}_2\text{B}_9\text{H}_{11}]^-$ in THF produces $[\text{3,3-(THF)}_2\text{-}i\text{closo-3,3'-Ln(3,1,2-LnC}_2\text{B}_9\text{H}_{11})_2]^-[\text{PPN}]^+$ ($\text{Ln} = \text{Sm}$ (**4**), Yb (**5**)), which has been characterized spectroscopically. The molecular structure of **4** has been established by an X-ray diffraction study. The complex **4** crystallizes in the triclinic space group *P* $\bar{1}$ with $a = 8.9374$ (3) Å, $b = 17.8703$ (6) Å, $c = 18.4989$ (7) Å, $\alpha = 107.5402$ (9)°, $\beta = 91.085$ (1)°, $\gamma = 90.705$ (1)°, $V = 2816$ Å³, and $Z = 2$. Data were collected at 25 °C on a diffractometer equipped with a small Huber circle, using Mo K α radiation, to a maximum of $2\theta = 45^\circ$, giving 7358 unique reflections, and the structure was solved by a combination of conventional Patterson, Fourier, and full-matrix least-squares techniques. The final discrepancy index was $R = 0.053$, $R_w = 0.065$ for 5324 independent reflections with $I > 3\sigma(I)$. Both the dicarbollide ligands are η^2 -bound to the Sm ion in a nonparallel or bent fashion, and the coordination sphere about the Sm is completed by two THF molecules. The coordination geometry of **4** can be best described as a distorted tetrahedron. This is the first structurally authenticated example of a bis(dicarbollide)lanthanide complex. The structure of **4** is compared with related bis(cyclopentadienyl)lanthanides.

Introduction

Recognition of the isolobal analogy between the cyclopentadienyl anion, $[\text{C}_5\text{H}_5]^-$, and the dicarbollide dianion, $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{11}]^{2-}$ (**1**), laid the foundation for the field of metallacarborane chemistry.¹ Dicarbollide complexes have been synthesized with a wide range of metals (d-transition series,² main group,³ 5f block⁴), but there have been no previous reports of any complexes of the dicarbollide ligand with metals of the 4f block.⁵

Synthesis of the uranium complex $[\text{Li}(\text{THF})_4]_2[\text{3,3-(Cl)}_2\text{-}i\text{closo-3,3'-U(3,1,2-UC}_2\text{B}_9\text{H}_{11})_2]^{4-}$ suggested that dicarbollide complexes of the lanthanides might be viable synthetic targets. Herein we report the synthesis of a new class of organolanthanide complexes, the *closo*-lanthanacarboranes. Both mono- and bis(di-

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