Anal. Calcd for $C_{32}H_{60}CdCl_2O_{12}P_4Ru_2$ (M_r = 1146.2): Cd, 9.81; Cl, 6.19; P, 10.81. Found: Cd, 9.94; Cl, 5.98; P, 10.64. Calcd for $C_{32}H_{60}Cl_2O_{12}P_4PbRu_2$ (M_r = 1241.0): C, 30.97; H, 4.87. Found: C, 30.87 H, 4.85.

$[\{(C_6Me_6)RuCl[P(O)(OCH_3)_2]_2\}_2M]PF_6$ ($[ML_2]PF_6$, $M^{3+} = Al^{3+}$, $Fe_3{}^+$). The compounds were prepared from **5** and $Al(NO_3)_3{\cdot}9H_2O$ or $FeCl_3{\cdot}6H_2O$ in water or water/methanol as described above. An excess of $NaPF_6$ was added to precipitate the salts completely. The yield was 60–80%. The products were recrystallized from chloroform/ether or acetone/ether to give fine black crystals of $[FeL_2]PF_6$ and yellow crystals of $[AlL_2]PF_6$.

Anal. Calcd for $C_{32}H_{60}AlCl_2F_6O_{12}P_5Ru_2$ (M_r = 1205.7): C, 31.88; H, 5.02. Found: C, 32.0; H, 5.26. Calcd for $C_{32}H_{60}Cl_2F_6FeO_{12}P_5Ru_2$ (M_r = 1234.6): C, 31.13; H, 4.82. Found: C, 31.13; H, 4.96.

$[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2Ru(C_6Me_6)]PF_6$ ($[LRu(C_6Me_6)]PF_6$). To a solution of 0.243 mmol of $Na[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2]$ (**5**, NaL) in methanol/water was added a solution of 0.121 mmol of $[\{(C_6Me_6)RuCl_2\}_2]$ in methanol. Slow addition of a concentrated solution of NH_4PF_6 in water gave a yellow precipitate, which was separated, washed with water, and dried under high vacuum. Recrystallization from acetone/ether gave orange-red crystals, yield 210 mg (93%).

^1H NMR (80 MHz, $CDCl_3$): δ 2.08 (s, 18 H, $C_6(CH_3)_6RuL$).

Anal. Calcd for $C_{28}H_{48}ClF_6O_6P_3Ru_2$ (M_r = 925.2): C, 36.35; H, 5.23. Found: C, 36.28; H, 5.35.

$[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2Rh(C_5Me_5)]PF_6$ ($[LRh(C_5Me_5)]PF_6$) and $[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2Ru(p\text{-}CH_3C_6H_4CH(CH_3)_2)]PF_6$ ($[LRu(p\text{-cymene})]PF_6$). The compounds were prepared as described for $[LRu(C_6Me_6)]PF_6$ from $[\{(C_5Me_5)RhCl_2\}_2]$ and $[\{(p\text{-cymene})RuCl_2\}_2]$ in 80–90% yield. $[LRh(C_5Me_5)]PF_6$ was characterized as follows.

^1H NMR (80 MHz, $CDCl_3$): δ 1.62 (s, 15 H, $C_5(CH_3)_5$).

Anal. Calcd for $C_{26}H_{45}ClF_6O_6P_3RhRu$ (M_r 900.0): C, 34.70; H, 5.04. Found: C, 34.64; H, 5.11.

$[LRu(p\text{-cymene})]PF_6$ was characterized as follows.

^1H NMR (80 MHz, $CDCl_3$): δ 1.34 (d, $^3J(HCCH)$ = 6.8 Hz, 6 H, $CH(CH_3)_2$), 2.23 (s, 3 H, $C_6H_4CH_3$), 2.85 (sept, $^3J(HCCH)$ = 6.8 Hz, 1 H, $CH(CH_3)_2$), 5.40 (m, 4 H, C_6H_4).

Anal. Calcd for $C_{26}H_{44}ClF_6O_6P_3Ru_2$ (M_r 897.1): C, 34.81; H, 4.94. Found: C, 34.63; H, 5.14.

$[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2Re(CO)_3]$ ($LRe(CO)_3$). A 79-mg amount (0.19 mmol) of $[ReBr(CO)_5]$ and 101 mg (0.19 mmol) of complex **6** (HL) in 30 mL of chloroform were heated to reflux under a nitrogen atmosphere for 24 h. The solution was concentrated and chromatographed on a short silica column. A yellow band was eluted with chloroform/acetone (20:1). Evaporation of the solvent and recrystallization from chloroform/pentane gave 103 mg (0.13 mmol, 67%) of orange-yellow crystals. The compound $LRe(CO)_3$ is stable in air, soluble in acetone, dichloromethane, chloroform, and THF, and insoluble in saturated hydrocarbon solvents.

Anal. Calcd for $C_{19}H_{30}ClO_9P_2ReRu$ (M_r = 787.1): C, 28.99; H, 3.84. Found: C, 28.83; H, 3.79.

IR (CH_2Cl_2, $\nu(CO)$): 2018 (st), 1889 (st, br) cm^{-1}.

$[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2Mo(CO)_3H]$ ($LMo(CO)_3H$). A 63-mg amount (0.21 mmol) of $[Mo(CH_3CN)_3(CO)_3]$ as added to a solution of 108 mg (0.21 mmol) of **6** in dichloromethane. The reaction mixture was stirred under nitrogen for 30 min and then filtered. Slow evaporation of the solvent gave 133 mg (92%) of large yellow to brown air-sensitive crystals.

IR (CH_2Cl_2, $\nu(CO)$): 2007 (st), 1915 (st), 1884 (m) cm^{-1}.

^1H NMR (80 MHz, CD_2Cl_2): δ −4.4 (s, Mo–H).

$[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2W(CO)_3H]$ ($LW(CO)_3H$). This compound was prepared in a manner analogous to that for $LMo(CO)_3H$ from 108 mg (0.21 mmol) of $[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}\{P(OH)(OCH_3)_2\}]$ (HL) and 101 mg (0.21 mmol) of $[W(DMF)_3(CO)_3]$; yield 159 mg (97%) of large yellow to brown air-sensitive crystals.

IR (CH_2Cl_2, $\nu(CO)$): 1994 (st), 1899 (st), 1872 (sh), 1845 (m) cm^{-1}.

^1H NMR (80 MHz, CD_2Cl_2): δ −3.4 (t, $^3J(POWH)$ = 1.3 Hz, satellites with $^1J(WH)$ = 10.4 Hz, W–H).

^{13}C NMR (67.9 MHz, $CDCl_3$): δ 16.0 (q, $^1J(CH)$ = 104 Hz, CCH_3), 51.3 (q, $^1J(CH)$ = 146 Hz, OCH_3), 51.7 (q, $^1J(CH)$ = 146 Hz, OCH_3), 104.9 (s, CCH_3), 218.4 (d, $^2J(CWH)$ = 16.0 Hz, satellites with $^1J(^{183}WC)$ = 154 Hz, $C{\equiv}O$).

Acknowledgment. Support of this research by the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen is gratefully acknowledged. We thank B. Engels, P. Dharmawan, and T. Schmitz for skillful experimental assistance. We are indebted to Bayer AG, Leverkusen, FRG, for a gift of trimethyl phosphite and dimethyl phosphonate and to Degussa AG, Frankfurt, FRG, for a loan of $RhCl_3{\cdot}aq$ and $RuCl_3{\cdot}aq$. W.K. thanks the Fonds der Chemischen Industrie for the continuous support of his work.

Note Added in Proof. The perchlorate salt of $[(C_6Me_6)RuCl\{P(OCH_3)_3\}_2]^+$ and compound **1** have recently been prepared in a similar way: Rojas, A.; Scotti, M.; Valderrama, M. *Bol. Soc. Chil. Quim.* **1988**, *33*, 103.

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Reactions of Arenediazonium Salts with Hexacarbonyldicobalt Derivatives. Synthesis of Cationic *N*-Aryldiazadicobaltatetrahedranes and Crystal and Molecular Structure of $[Co_2(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}N_2C_6H_4\text{-}4\text{-}CH_3)][SbF_6]$

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$Co_2(CO)_4(\mu\text{-}CO)_2(\mu\text{-dppm})$ (dppm = bis(diphenylphosphino)methane) reacts with a variety of arenediazonium salts in dichloromethane at temperatures well below ambient to produce a series of novel *N*-aryldiazadicobaltatetrahedrane cations as their $[BF_4^-]$, $[PF_6^-]$, and $[SbF_6^-]$ salts. The spectroscopic characterizations of these new compounds are discussed, and the structure of $[Co_2(CO)_4(\mu\text{-}N_2C_6H_4\text{-}4\text{-}CH_3)(\mu\text{-dppm})][SbF_6]$ has been determined by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group *Pbca*, with unit cell dimensions *a* = 22.488 (5) Å, *b* = 19.459 (4) Å, *c* = 18.002 (4) Å, *V* = 7877 (3) Å^3, and *Z* = 8. The structure refined to *R*(*F*) = 5.40%. It is an isolobal analogue of tetrahedrane; the distorted tetrahedral Co_2N_2 core contains a 1.342 (12) Å N–N bond (midway between a single and a double bond) and a Co–Co distance of 2.440 (2) Å.

Introduction

Since the first report more than 20 years ago,[2] reactions of arenediazonium ions with nucleophilic transition-metal compounds have produced a profusion of neutral, monocationic, and even dicationic aryldiazenyl and aryldiazene derivatives of most of the transition metals.[3] A rather small subset involves the ArN_2 moiety

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(1) (a) University of Minnesota—Duluth. (b) University of Delaware.

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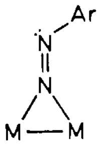
Table I. FABMS and IR (ν_{CO}) Data for [**6**][BF_4][a]

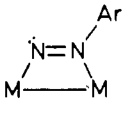
cation	molecular ion,[b] *m/e*	high-res FABMS, *m/e*		ν_{CO},[c] cm^{-1}
		obsd	calcd	
6a$^+$	764	763.9973	763.9961	2087, 2070, 2051
6b$^+$	737	736.9991	737.0015	2086, 2068, 2047
6c$^+$	719	719.0155	719.0109	2086, 2067, 2046
6d$^+$	733	733.0243	733.0265	2085, 2066, 2045
6e$^+$	761	761.0609	761.0580	2085, 2067, 2045
6f$^+$	749	749.0202	749.0214	2084, 2066, 2044

[a] [**6a-f**$^+$] = [$Co_2(CO)_4(p\text{-}XC_6H_4N_2)(dppm)^+$]: X = NO_2, **6a**; X = F, **6b**; X = H, **6c**; X = CH_3, **6d**; X = $CH(CH_3)_2$, **6e**; X = OCH_3, **6f**. [b] All spectra also exhibit ions resulting from sequential loss of four CO ligands and N_2. The ions $(M - n\text{CO} + H)^+$ are also prominent. [c] In CH_2Cl_2 solution.

bound to more than one metal center;[4,5] three structural types have been characterized.[5] In structures **1** and **2**, the (neutral) ArN_2

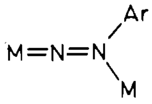


1



2

fragment functions as a 3-electron donor to the dimetal unit. In structure **3**, where a metal–metal bond is precluded, the (neutral) ArN_2 is a 5-electron donor. Structural type **4**, in which ArN_2 is a 5-electron donor to a metal–metal-bonded dimetal unit has been unknown hitherto. The diazadimetallatetrahedrane core bears an obvious resemblance to structure **5**, numerous examples of which have been reported,[6] as well as to $[Co(CO)_3]_2P_2$[7] and $[Co(CO)_3]_2As_2$.[8] We now report the syntheses and characterizations, including a single-crystal X-ray diffraction study, of a series of cations [**6**$^+$], the first N-aryldiazadicobaltatetrahedrane cations.



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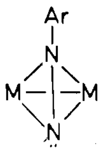

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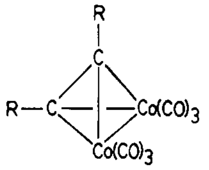

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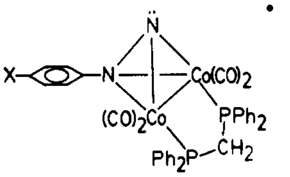

6a, X=NO_2
6b, X=F
6c, X=H
6d, X=CH_3
6e, X=$CH(CH_3)_2$
6f, X=OCH_3

Table II. NMR Data for [**6**][PF_6][a]

cation	chem shift, ppm: ^1H NMR[b]	chem shift, ppm: $^{31}P\{^1H\}$ NMR[c]
6a$^+$	4.92 ("t", $^2J_{PH}$ = 12.1 Hz)[d]	39.67
6b$^+$	4.84 ("t", $^2J_{PH}$ = 12.0 Hz)[d]	39.19
6c$^+$	4.80 ("t", $^2J_{PH}$ = 11.9 Hz)[d]	38.90
6d$^+$	4.78 (d, H_A), 4.72 (d, H_B); J_{AB} = 13.4 Hz[e] 2.40 (s, $C_6H_4CH_3$)	39.31
6e$^+$	4.86 (d, H_A), 4.79(d, H_B); J_{AB} = 13.7 Hz[e] 3.03 (sept, $CH(CH_3)_2$), 1.26 (d, $CH(CH_3)_2$); $^3J_{HH}$ = 7 Hz	38.95
6f$^+$	4.75 (d, H_A), 4.68 (d, H_B); J_{AB} = 13.7 Hz[e] 3.91 (s, $C_6H_4OCH_3$)	39.29

[a] In CD_2Cl_2 and $(CD_3)_2CO$. [b] Phenyl resonances not listed (see text). [c] All spectra also include PF_6^- resonance (−144.4 ppm (sept, $^1J_{PF}$ = 706 Hz)). Resonances for Co-bound P are broadened (fwhm ca. 110 Hz) by ^{59}Co (I = $^7/_2$, 100%). [d] Recorded without selective ^{31}P irradiation. [e] Recorded with selective ^{31}P irradiation.

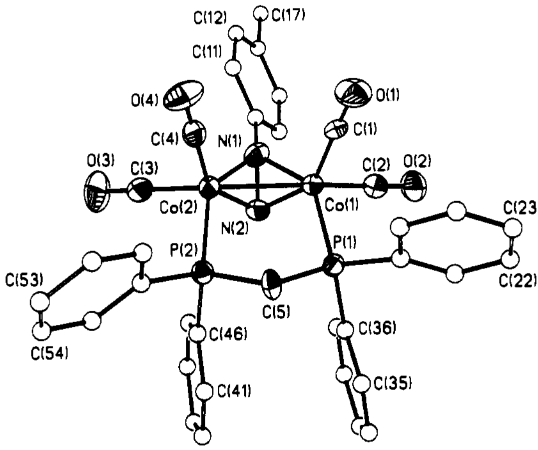

Figure 1. Structure and labeling scheme for the cation of [**6d**][SbF_6]. Thermal ellipsoids are drawn at the 45% level, and the phenyl rings are drawn with arbitrary radius spheres.

Results

$Co_2(CO)_4(\mu\text{-}CO)_4(\mu\text{-dppm})$[9] reacts with arenediazonium salts, [$p\text{-}XC_6H_4N_2^+$][A^-] (X = NO_2, F, H, CH_3, $CH(CH_3)_2$, OCH_3; [A^-] = [BF_4^-], [PF_6^-], [SbF_6^-]) at temperatures below 0 °C to produce salts of the cations [**6**$^+$] (see Experimental Section). These compounds are moderately air-stable, deep red-purple crystalline solids that dissolve in acetone, dichloromethane, acetonitrile, and, to a smaller extent, tetrahydrofuran, to give air-sensitive solutions. They are insoluble in aromatic and aliphatic hydrocarbons, and they decompose without melting or subliming.

Their low-resolution FAB mass spectra exhibit molecular ions and sequential loss of four CO ligands and N_2. High-resolution peak matches on the molecular ions confirm the formulations [$Co_2(CO)_4(N_2C_6H_4X)(dppm)^+$] (Table I).

Their IR spectra (Table I) are devoid of absorptions in the bridging CO region, and the absorptions in the terminal CO region are 40–50 cm^{-1} to high frequency of those in the IR spectrum of $Co_2(CO)(\mu\text{-}CO)_2(\mu\text{-dppm})$. The former also show a small, but systematic, variation with para substituent X.

The $^{31}P\{^1H\}$ NMR spectra (Table II) of cations [**6**$^+$] consist of a single resonance each, down to −90 °C. These resonances are rather broad at room temperature (fwhm ca. 110 Hz), but narrow as the probe temperature is lowered (fwhm ca. 35 Hz at

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–60 °C). The chemical shifts are neither greatly nor systematically dependent on X.

In addition to resonances in the expected regions for P–Ph and N–Ar protons and for X protons (**6d–f**), the ^{1}H NMR spectra (Table II) feature PCH_2P multiplets whose chemical shifts are neither greatly nor systematically dependent on X. These are discussed further below.

In part because of the novelty of the structure implied by the spectroscopic data, we undertook a single-crystal X-ray diffraction study of [**6d**][SbF_6].

Structure Description

[$Co_2(CO)_4(\mu$-N_2-$C_6H_4CH_3)(\mu$-dppm)][SbF_6] ([**6d**][SbF_6]) crystallizes as well-separated ions without significant interionic contacts. The cation structure (Figure 1) contains a central distorted tetrahedral Co_2N_2 core with a short N–N bond, 1.342 (12) Å, a Co–Co distance of 2.440 (2) Å and average Co–N distances of 1.898 (8) Å to the substituted N atom and 1.939 (8) Å to the other N atom. An equivalent description of the Co_2N_2 core considers it to be a complex of the N≡N triple bond to the Co_2 moiety. Assignment of a specific coordination geometry to Co is difficult due to the very acute N–Co–N angles, 41.0 (3)° (average). The dppm ligand bridges the two Co atoms.

The N–N distance of 1.342 (12) Å is considerably longer than the N=N double bonds in (μ-H)$Os_3(CO)_{10}(\mu,\eta^2$-N=NPh) (1.20 (4) Å),[5d] (μ-H)$Os_3(CO)_{10}(\mu,\eta^1$-N=N-p-Tol) (1.238 (18) Å),[5c] [$Mn(CO)_4(\mu,\eta^1$-N=NPh)]$_2$ (1.233 (2) Å)[5a] CH_3N=NCH_3 (1.23 Å),[10] and FN=NF (1.25 (4) Å).[11] It is somewhat shorter than the distances in compounds such as [$(CH_3)_3CCN]_2Ni(\eta^2$-PhN=NPh) (1.385 (5) Å),[12] $Fe_2(CO)_6(\mu,\eta^2$-CH_3N=NCH_3) (1.366 (8) Å),[13] $Fe_2(CO)_6(\mu,\eta^2$-$C_{12}H_8N_2$) (1.399 (8) Å),[14] and $Fe_2(CO)_6(\mu,\eta^2$-$C_5H_8N_2$) (1.404 (9) Å),[15] in which the N=N π electrons are necessarily involved in bonding to the metal centers. It is substantially shorter than the 1.45 Å distance in hydrazine, which may be taken as representative of a N–N single bond.[16] The N–N distance in our compound is thus consistent with substantial reduction in the N–N bond order, from 3 in the starting diazonium ion to between 1 and 2 in the product.

The Co–Co distance is unusually short for Co_2E_2 (E = group 15 element) tetrahedranes. In the Co_2As_2 complex $Co_2(CO)_5$-[$P(C_6H_5)_3$](μ-As_2), the Co–Co distance is 2.594 (3) Å; it is 2.576 (3) Å in $Co_2(CO)_4[P(C_6H_5)_3]_2(\mu$-$As_2$)[8] and 2.574 (3) Å in $Co_2(CO)_5[P(C_6H_5)_3](\mu$-$P_2$);[7] in the cubane analogue [$Co_4(\eta^5$-$C_5H_5)_4P_4$] the Co–Co distance is 2.504 Å (average).[17]

Discussion

Solution Structures of [6$^+$] from Spectroscopic Data. The appearance of terminal CO ligand absorptions at frequencies 40–50 cm^{-1} higher than the corresponding absorptions in $Co_2(CO)_4(\mu$-$CO)_2(\mu$-dppm) is consistent with a single positive charge delocalized over two Co centers.[18] Further, the small but systematic dependence of ν_{CO} on X in cations [**6**$^+$] indicates that information about the electronic characteristics of X is being transmitted through the N-aryl ring and through the N–N moiety to the Co centers and thence to the CO ligands.

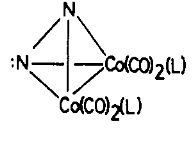
The presence of a single resonance in the $^{31}P\{^1H\}$ NMR spectrum of each cation indicates the presence of a plane of symmetry relating the two dppm phosphorus sites. There is no evidence for fluxional behavior giving this result in the temperature range we examined (–90 to +20 °C). The phosphorus resonances *narrow* as the probe temperature is lowered; this observation is consistent with their admittedly rather large line widths at room temperature being due to the proximity of quadrupolar ^{59}Co ($I = {}^7/_2$, 100%) nuclei. As the temperature is lowered, slower molecular motions increase τ_C, the correlation time, which, in turn, decreases T_Q, the quadrupolar relaxation time, effectively decoupling the ^{31}P nucleus from the quadrupolar ^{59}Co nuclei.[19]

Table III. Crystal, Data Collection, and Refinement Parameters for [**6d**][SbF_6]

formula	$C_{36}H_{29}Co_2F_6$-$N_2O_4P_2Sb$	Z	8
		D(calcd), g cm^{-3}	1.634
fw	969.14	size, mm	0.20 × 0.31 × 0.43
cryst system	orthorhombic		
space group	*Pbca*	color	purple
a, Å	22.488 (5)	temp, K	293
b, Å	19.459 (4)	T_{max}/T_{min}	0.260/0.215
c, Å	18.002 (4)	μ, cm^{-1}	16.6
V, Å^3	7877 (3)	scan method	Wyckoff
diffractometer	Nicolet R3m	no. of data colld	6052
radiation	Mo Kα	no. of indep data	5486
wavelength, Å	$\lambda = 0.71073$	no. of obsd data ($5\sigma F_o$)	2747
monochromator	graphite		
scan limits, deg	$4 \le 2\theta \le 45$	std reflcns	3 stds/197 reflcns
scan speed, deg min^{-1}	variable, 5–20		
data collected	$+h, +k, +l$	decay, %	<2
$R(F)$, %	5.40	Δ/σ	0.014
$R_w(F)$, %	6.21	$\Delta(\rho)$, eÅ^{-3}	0.55
GOF	1.22	N_o/N_v	8.86

For purposes of discussion, the ^{1}H NMR spectra of cations [**6**$^+$] may be divided into three regions. The "X" regions are featureless in the spectra of **6a–c**, and they show the expected resonances for the p-CH_3, p-$CH(CH_3)_2$, and p-OCH_3 groups in the spectra of **6d–f**, respectively. The aromatic regions, which contain resonances due to the protons on the N-aryl rings as well as resonances due to the protons on the (pairwise diastereotopic) P–Ph rings, are extremely crowded and complex. They are, accordingly, of no diagnostic value, apart from showing relative integrations compatible with the formulations of [**6**$^+$]. The chemical shifts of the dppm methylene protons do not vary systematically with the N-aryl para-substituent X. On the other hand, the PCH_2P regions of the ^{1}H NMR spectra of [**6**$^+$] fall into two distinct groups according to the size of the chemical shift *difference* between the two diastereotopic methylene protons. In one group, consisting of the spectra of **6d–f**, these chemical shift differences are sufficient to make these methylene protons clearly the AB portions of ABX_2 spin systems. Selective ^{31}P irradiation collapses the multiplets to AB quartets. In the other group, consisting of the spectra of cations **6a–c**, these chemical shift differences are either too small to resolve, even at 300 MHz, or (fortuitously) absent. Selective ^{31}P irradiation collapses these "triplets" to "singlets". Although we do not understand the origin of this dichotomy, we do note that isochronous diastereotopic protons have precedent in compounds with substituted cyclopentadienyl rings.[20]

The bonding in **5** has been examined by extended Hückel methods;[21] the same sort of calculation led the same group to the conclusion that the diazadicobaltatetrahedrane **7** should be stable.[22]



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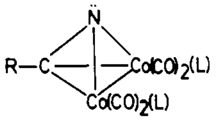

8

Structure **6** has not been investigated theoretically, but the results we have described are experimental evidence of its stability. They raise the intriguing possibility that other variations on this theme, such as azadicobaltatetrahedranes derived from nitriles (e.g., **8**)

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Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 $\times$ 10^3) for [**6d**][SbF_6]

	x	*y*	*z*	*U*[a]
Sb	917.7 (4)	3788.1 (5)	1895.6 (5)	63.2 (3)
Co(1)	2653.1 (6)	5122.3 (7)	−434.5 (8)	37.6 (5)
Co(2)	2433.0 (6)	6029.0 (7)	460.8 (8)	39.7 (5)
P(1)	1749 (1)	5034 (1)	−932 (2)	37 (1)
P(2)	1492 (1)	6193 (2)	108 (2)	39 (1)
F(1)	1544 (4)	3582 (7)	2483 (7)	196 (7)
F(2)	430 (4)	3280 (5)	2519 (5)	124 (4)
F(3)	286 (4)	4075 (6)	1332 (6)	164 (6)
F(4)	793 (6)	4540 (5)	2470 (6)	180 (6)
F(5)	1395 (3)	4310 (4)	1264 (4)	90 (3)
F(6)	1030 (7)	3050 (5)	1330 (7)	227 (8)
N(1)	3165 (4)	5778 (4)	12 (5)	54 (3)
N(2)	2827 (3)	6093 (4)	−499 (5)	50 (3)
O(1)	2663 (4)	3848 (5)	437 (5)	88 (4)
O(2)	3282 (4)	4545 (5)	−1713 (5)	78 (4)
O(3)	2580 (5)	7376 (5)	1161 (6)	116 (5)
O(4)	2307 (4)	5249 (5)	1855 (5)	95 (4)
C(1)	2654 (5)	4347 (6)	112 (6)	48 (4)
C(2)	3034 (5)	4771 (6)	−1222 (7)	45 (4)
C(3)	2536 (5)	6867 (6)	885 (6)	62 (5)
C(4)	2339 (5)	5546 (7)	1307 (7)	53 (5)
C(5)	1193 (4)	5376 (5)	−283 (6)	44 (4)
C(11)	4039 (5)	5758 (7)	774 (7)	72 (5)
C(12)	4659 (5)	5797 (7)	830 (7)	77 (6)
C(13)	5012 (5)	5962 (6)	237 (7)	66 (5)
C(14)	4741 (5)	6055 (6)	−435 (7)	73 (5)
C(15)	4124 (4)	6005 (6)	−518 (6)	56 (4)
C(16)	3791 (4)	5863 (5)	94 (6)	39 (4)
C(17)	5679 (5)	5996 (7)	302 (8)	96 (7)
C(21)	1651 (3)	3864 (4)	−1802 (4)	57 (3)
C(22)	1585	3159	−1916	76 (4)
C(23)	1393	2738	−1336	76 (4)
C(24)	1269	3023	−642	83 (4)
C(25)	1335	3728	−528	66 (4)
C(26)	1527	4148	−1108	43 (3)
C(31)	2047 (2)	5905 (4)	−2097 (4)	45 (3)
C(32)	1933	6262	−2753	65 (4)
C(33)	1383	6196	−3103	73 (4)
C(34)	946	5773	−2797	79 (4)
C(35)	1060	5415	−2141	55 (3)
C(36)	1610	5481	−1791	37 (3)
C(41)	861 (3)	6902 (4)	−974 (4)	60 (3)
C(42)	794	7387	−1538	72 (4)
C(43)	1269	7813	−1730	69 (4)
C(44)	1811	7754	−1357	60 (4)
C(45)	1877	7269	−793	49 (3)
C(46)	1403	6843	−601	39 (3)
C(51)	771 (3)	5899 (3)	1318 (4)	66 (4)
C(52)	349	6050	1862	75 (4)
C(53)	112	6711	1912	67 (4)
C(54)	297	7221	1419	90 (5)
C(55)	719	7070	875	70 (4)
C(56)	956	6409	825	41 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

or isonitriles may be stable, as well. Their absence from the literature may be due to the lack (to date) of a suitable means of synthesis.

Experiments aimed at defining the further reactivities of [**6**$^+$] and the mechanism of their formation are in progress, and will be reported in due course.

Experimental Section

General Data. All reactions and manipulations involving air-sensitive materials were carried out under an atmosphere of dry N_2 in oven-dried glassware, using solvents dried by standard methods.[23]

$Co_2(CO)_6$(dppm)[8] and arenediazonium salts[24] were prepared by published procedures; $Co_2(CO)_8$ (Strem), $Ph_2PCH_2PPh_2$ (Aldrich), and anilines (Aldrich) were obtained commercially.

Table V. Selected Bond Parameters for [**6d**][SbF_6]

(a) Bond Distances (Å)

Co(1)–Co(2)	2.440 (2)	Co(2)–C(3)	1.816 (12)
Co(1)–P(1)	2.227 (3)	Co(2)–C(4)	1.803 (12)
Co(2)–P(2)	2.232 (3)	C(1)–O(1)	1.134 (15)
Co(1)–N(1)	1.898 (9)	C(2)–O(2)	1.134 (15)
Co(2)–N(1)	1.898 (9)	C(3)–O(3)	1.112 (15)
Co(1)–N(2)	1.932 (8)	C(4)–O(4)	1.145 (15)
Co(2)–N(2)	1.945 (8)	P(1)–C(5)	1.837 (11)
N(1)–N(2)	1.342 (12)	P(2)–C(5)	1.864 (10)
Co(1)–C(1)	1.801 (12)	Sb–F (av)	1.825 (16)
Co(1)–C(2)	1.792 (12)		

(b) Bond Angles (deg)

Co(1)–N(1)–Co(2)	80.0 (3)	C(2)–Co(1)–N(1)	107.6 (4)
Co(1)–N(2)–Co(2)	78.0 (3)	C(1)–Co(1)–N(2)	148.3 (4)
P(1)–Co(1)–N(1)	140.9 (3)	C(2)–Co(1)–N(2)	103.2 (4)
P(1)–Co(1)–N(2)	103.6 (2)	C(3)–Co(2)–N(1)	107.4 (5)
P(2)–Co(2)–N(1)	137.6 (3)	C(4)–Co(2)–N(1)	109.1 (5)
P(2)–Co(2)–N(2)	99.8 (2)	C(3)–Co(2)–N(2)	104.9 (4)
P(1)–Co(1)–C(1)	99.0 (4)	C(4)–Co(2)–N(2)	146.9 (5)
P(1)–Co(1)–C(2)	95.1 (4)	C(1)–Co(1)–C(2)	96.4 (5)
P(2)–Co(2)–C(3)	96.4 (4)	C(3)–Co(2)–C(4)	94.4 (5)
P(2)–Co(2)–C(4)	101.8 (4)	Co(1)–P(1)–C(5)	109.7 (3)
N(1)–Co(1)–N(2)	41.0 (4)	P(1)–C(5)–P(2)	107.6 (5)
N(1)–Co(2)–N(2)	40.9 (3)	Co(2)–P(2)–C(5)	109.2 (3)
C(1)–Co(1)–N(1)	109.3 (4)		

NMR. ^{1}H NMR spectra were obtained at 200 MHz on an IBM/Bruker NR 200 AF instrument or at 300 MHz on a Nicolet NTC 300 spectrometer and were referenced internally to residual solvent protons. Chemical shifts are reported in ppm downfield from external Me_4Si. ^{31}P NMR spectra were obtained at 81 MHz on the NR 200 AF instrument or at 121.5 MHz on the NTC 300 instrument and were referenced internally to NH_4PF_6 or externally to $P(OCH_3)_3$ by sample replacement. Chemical shifts are reported in ppm downfield from external 85% aqueous H_3PO_4. Variable-temperature NMR spectra were obtained on the NR 200 AF instrument by using a Bruker VT-1000 temperature controller.

Other Spectra. IR spectra were obtained on Beckman IR-12 and Perkin-Elmer PE781 instruments. FAB mass spectra were obtained on the Kratos MS-50 Triple Analyzer instrument at the Midwest Center for Mass Spectrometry.

Syntheses of [$Co_2(CO)_4(\mu\text{-}N_2C_6H_4X)(\mu\text{-dppm})^+$] Salts. Apart from the temperatures at which the color changes occurred, the syntheses of the cations [**6**$^+$] are much the same; accordingly, only the preparation of [**6a**][BF_4] is given in full detail. The temperatures and the isolated yields of [**6**][BF_4] are summarized as follows: (cation, approximate temperature for appearance of brown color, approximate temperature for appearance of purple color, yield as [BF_4^-] salts): [**6a**$^+$], −70 °C, −60 °C, 53.6%; [**6b**$^+$], −60 °C, −45 °C, 59.2; [**6c**$^+$], −50 °C, −35 °C, 47.6%; [**6d**$^+$], −35 °C, −25 °C, 69.1%; [**6e**$^+$], −35 °C, −25 °C, 40.7%; [**6f**$^+$], −25 °C, −5 °C, 52.7%. The [PF_6^-] and [SbF_6^-] salts may be prepared analogously, starting with the appropriate arenediazonium salts.

Combustion analyses of the [BF_4^-] salts are given in Table S6. Consistently low results were obtained for N, and in some cases, high results were obtained for H and P; accordingly, the characterizations of the salts of [**6**$^+$] rest upon their spectroscopic data and the single-crystal x-ray diffraction study of [**6d**][SbF_6].

[$Co_2(CO)_6(\mu\text{-}N_2C_6H_4NO_2)(\mu\text{-dppm})$][$BF_4$]. $Co_2(CO)_6(\mu$-dppm)(452.3 mg, 0.6748 mmol) was dissolved in dry dichloromethane (25 mL) and the solution was cooled to −78 °C. Solid [p-$NO_2C_6H_4N_2$][BF_4] (165.5 mg, 0.6985 mmol) was added against a brisk N_2 flow. The mixture was stirred and warmed slowly; at −70 °C, the color changed from orange to brown and, at −60 °C, to the deep red-purple characteristic of the product cation. The temperature was maintained at −60 °C for 4 h, after which time the solution was filtered through a Celite pad under nitrogen to remove a small amount of insoluble solid. The filtrate was concentrated to 15 mL and then layered with dry hexane. This was set aside at −30 °C for 2–3 days, during which time purple crystals deposited. These were isolated by cannula filtration, washed with hexane (3 × 10 mL), and dried under vacuum (295.5 mg, 0.347 mmol, 53.6%).

X-ray Structural Determination. The crystallographic parameters for [**6d**][SbF_6] are given in Table III. The crystals were all irregularly shaped; therefore, no characterizing adjective could be ascribed to the crystal habit. Preliminary photographic characterization revealed *mmm* Laue symmetry. Systematic absences in the reflection data unambiguously indicated the orthorhombic space group *Pbca*. The unit cell dimensions were obtained from the least squares fit of the angular settings

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of 25 reflections (24° ≤ 2θ ≤ 29°). An empirical absorption correction (ψ-scan, six reflections–216 data, at 10° increments about the diffraction vector pseudoellipsoid model) was applied to the data.

Direct methods provided the initial Sb, Co, and P atom positions; the structure was completed by difference Fourier syntheses. The P-bonded phenyl rings were constrained to rigid, planar hexagons (C–C = 1.395 Å) to conserve data. Hydrogen atoms were treated as idealized, updated contributions (C–H = 0.96 Å). All nonhydrogen atoms except for the carbon atoms of the dppm phenyl rings were refined with anisotropic thermal parameters.

SHELXTL (Version 5.1) software was used for all computations (Nicolet Corp., Madison, WI). The atomic coordinates are given in Table IV, and selected bond parameters are given in Table V.

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Supplementary Material Available: Listings of additional bond lengths (Table S2), additional bond angles (Table S3), anisotropic thermal parameters (Table S4), calculated hydrogen atom coordinates and isotropic thermal parameters (Table S5), and analytical data for [BF_4^-] salts (Table S6) (5 pages); listings of observed and calculated structure factors (Table S1) (17 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of Tris(trimethylsilyl)silyl and Tris(trimethylsilyl)germyl Derivatives of Zirconium and Hafnium. X-ray Crystal Structures of (η^5-C_5Me_5)$Cl_2HfSi(SiMe_3)_3$ and (η^5-C_5Me_5)$Cl_2HfGe(SiMe_3)_3$

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Received May 12, 1988

By reaction of $(THF)_3LiSi(SiMe_3)_3$ or $(THF)_3LiGe(SiMe_3)_3$ with the appropriate metal halide, the following silyl and germyl derivatives of zirconium and hafnium have been prepared: (η^5-C_5Me_5)$Cl_2MSi(SiMe_3)_3$ (M = Zr, Hf), (η^5-C_5H_5)$_2$Zr[Ge$(SiMe_3)_3$]Cl, and (η^5-C_5Me_5)$Cl_2MGe(SiMe_3)_3$ (M = Zr, Hf). In addition, the pyridine adduct (η^5-C_5Me_5)$Cl_2HfSi(SiMe_3)_3$(py) has been isolated from reaction of (η^5-C_5Me_5)$Cl_2HfSi(SiMe_3)_3$ with pyridine. (η^5-C_5Me_5)$Cl_2HfSi(SiMe_3)_3$ and (η^5-C_5Me_5)$Cl_2HfGe(SiMe_3)_3$ represent the first hafnium silyl and germyl complexes to be structurally characterized. Crystals of (η^5-C_5Me_5)$Cl_2HfSi(SiMe_3)_3$ are monoclinic, $C2/c$, with a = 39.62 (2) Å, b = 9.465 (5) Å, c = 17.255 (8) Å, β = 114.29 (4)°, V = 5897 (5) Å^3, Z = 8, R_F = 5.26%, and R_{wF} = 5.35%. (η^5-C_5Me_5)$Cl_2HfGe(SiMe_3)_3$ is isomorphous, with a = 39.74 (1) Å, b = 9.504 (3) Å, c = 17.313 (6) Å, β = 114.35 (3)°, V = 5956 (4) Å^3, Z = 8, R_F = 5.04%, and R_{wF} = 5.86%. The Hf–Si bond length in (η^5-C_5Me_5)$Cl_2HfSi(SiMe_3)_3$ is 2.748 (4) Å, and the Hf–Ge bond length in (η^5-C_5Me_5)$Cl_2HfGe(SiMe_3)_3$ is slightly shorter, at 2.740 (1) Å.

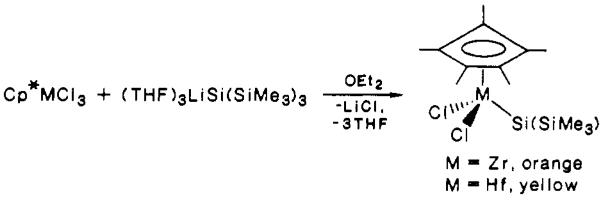
Introduction

Our investigations of early transition-metal silyl compounds have shown that the reactivity of early metal-silicon bonds can be dramatically influenced by changes of substituents at both the metal and silicon.[1] For example, whereas $Cp_2Zr(SiMe_3)Cl$[1a] (Cp = η^5-C_5H_5) and CpCp*Zr[$Si(SiMe_3)_3$]Cl[1b,e] (Cp* = η^5-C_5Me_5) combine rapidly with carbon monoxide to form η^2-$COSiR_3$ derivatives, $Cp_2Zr[Si(SiMe_3)_3]Cl$[1a] is unreactive toward CO under similar conditions. This implies that elucidation of structure–reactivity correlations can be very important in the development of this area. Presently studies directed toward this goal are complicated by the fact that relatively few early transition-metal silyl complexes have been described.[2] All reported zirconium and hafnium silyls are 16- or 18-electron metallocene derivatives of the type (η^5-C_5R_5)(η^5-$C_5R'_5$)M(SiR''_3)X (R, R' = H, Me). Clearly, thorough investigations of the chemistry of early transition-metal-silicon bonds will rely on efficient synthetic routes to a range of complexes.

We report here the synthesis and characterization of a new type of group 4 silyl derivative, the formally 12-electron species Cp*$Cl_2MSi(SiMe_3)_3$ (M = Zr, Hf). Initial investigations indicate that these derivatives possess M–Si bonds that are exceptionally reactive toward insertion of unsaturated substrates.[1d,3] The syntheses of new germyl complexes of zirconium and hafnium, $Cp_2Zr[Ge(SiMe_3)_3]Cl$ and Cp*$Cl_2MGe(SiMe_3)_3$ (M = Zr, Hf), are also described. The only previously reported germyl derivatives of zirconium and hafnium appear to be the complexes $Cp_2M(GePh_3)Cl$ (M = Zr, Hf).[4] The X-ray structures of Cp*$Cl_2HfSi(SiMe_3)_3$ and Cp*$Cl_2HfGe(SiMe_3)_3$ are the first to be determined for silyl- and germyl-hafnium complexes.

Results and Discussion

Metal silyl complexes Cp*$Cl_2MSi(SiMe_3)_3$ (M = Zr, Hf) are prepared by the reaction shown in eq 1. As solids, these silyl



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