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Pentamethylcyclopentadienyl Transition Metal Complexes. 9.[1] Reactions and Solid-State and Solution Behavior of Dinuclear Cobalt(II) Complexes $[C_5Me_5Co(\mu\text{-}X)]_2$

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Reaction of C_5Me_5Li (Cp*Li) with Co(II) halides, CoX_2 (X = Cl, Br, I), or the hexaammine $[Co(NH_3)_6](BF_4)_2$ in 1:1 molar ratio leads to binuclear Co(II) half-sandwich complexes $(Cp^*Co)_2(\mu\text{-}X)_2$ (**1**, X = Cl, Br, I, NH_2). Starting from **1a** and **1b** (X = Cl, Br), derivatives with the bridging ligands NMe_2, OEt, SMe, and PPh_2 are obtained. The stability of the compounds range from nearly air stable (X = SMe) to extremely air sensitive and thermally labile (X = I). Magnetic measurements show a strong antiferromagnetic interaction of the two d^7 Co centers. EPR, ^1H NMR, and electrochemical investigations were used to demonstrate a monomer/dimer equilibrium in solution. The binuclear halo compounds are cleaved by donor bases (pyridine and phosphines) to yield mononuclear complexes Cp*CoXL.

Introduction

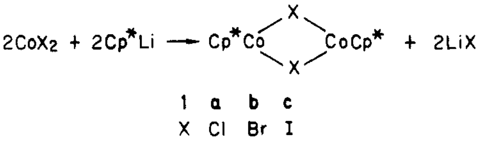
Cyclopentadienyl half-sandwich complexes of cobalt commonly are of the type $CpCoL_2$ or $[CpCoL_nX_{3-n}]^{(2-n)+}$ (n = 0–3), with formally Co(I) or Co(III) as the central metal. Recently the Co(II) types $[CpCoL_2]^+$ and CpCoLX,[2-4] where L is a phosphine, were isolated as the first examples of Co(II) half-sandwich complexes. We had found that when the cyclopentadienyl (Cp) is replaced by the pentamethylcyclopentadienyl (Cp*) ligand, complexes of composition Cp*CoX[5] are obtained under suitable conditions. These have been shown to undergo a variety of interesting reactions. Thus oxidation in the presence of an additional anionic ligand, Y^-, gives dinuclear Co(III) complexes $[Cp^*Co(\mu\text{-}X_2,Y)CoCp^*]^+$, which in turn are starting materials for a wide variety of mono- and binuclear (pentamethylcyclopentadienyl)cobalt(III) complexes including the aqua and hydroxy species $[Cp^*Co(H_2O)_3]^{3+}$ and $[Cp^*Co(\mu\text{-}OH)_3CoCp^*]^+$, respectively.[6] Valence disproportionation with either diolefins or CO in pentane leads to the molecular halo Co(III) complexes $[Cp^*CoX(\mu\text{-}X)]_2$ along with neutral Cp*Co(diolefin) or $Cp^*Co(CO)_2$, respectively.

Reaction of $[Cp^*CoX]_2$ with anionic cyclic π-ligands provides a route to mixed-sandwich complexes as is exemplified by the preparation of pentamethylcobaltocene.[5]

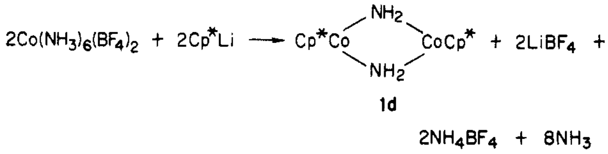
We have now extended the number of bridging ligands X in these complexes and have investigated their solid-state and solution behavior in more detail. We report also cleavage reactions with donor ligands (pyridine and phosphines) which yield mononuclear Co(II) complexes Cp*CoXL which, with respect to their magnetic behavior, serve as valuable reference compounds for their dinuclear precursors.

Results

Binuclear Complexes $[Cp^*Co(\mu\text{-}X)]_2$. Compounds **1a–c** were obtained from $CoCl_2$, $CoBr_2$·DME (DME = 1,2-dimethoxyethane) and CoI_2 by reaction with Cp*Li (1:1 molar ratio) in THF at −20 to 0 °C, in yields of up to 90% (e.g., **1a**). The formation of **1d** from $Co(NH_3)_6(BF_4)_2$ and Cp*Li (eq 1b) requires a 2-h reaction time at 40 °C. The chloride **1a** is thermally stable, but the bromide **1b** and the amide **1d** are less so and solutions of the iodide **1c** invariably tend to decompose with separation of CoI_2 even at low temperature. The intermediate formation of **1c** is proven by oxidizing the pentane extracts with iodine to yield the known Cp^*CoI_2.[6] The yield of **1d**, which is very soluble in pentane and crystallizes incompletely, is best determined by in situ reduction to $Cp^*Co(CO)_2$ according to eq 2.[5] The isolated yield of the dicarbonyl of >80%



(1a)



(1b)

$$\mathbf{1d} + n\mathrm{CO} \rightarrow 2\mathrm{Cp^*Co(CO)_2} + (\mathrm{CONH})_x \qquad (2)$$

indicates that also in this case the stoichiometry of the reaction is that of eq 1. This in turn indicates that the formation of the bridging NH_2 group must be effected by liberated ammonia rather than by Cp*Li. The use of cobalt hexaammine bis(tetrafluoroborate) instead of the more common (and more readily prepared) dichloride in reaction 1b is mandatory in order to prevent the formation of mixed amido/chloro species. Complexes **1** form dark brown (**1a–c**) or green (**1d**) solutions in all common polar and unpolar solvents, which are extremely air sensitive. Solutions and solids are paramagnetic.

Exchange of Bridging Ligands in 1a and 1b. Derivatives of type **1** are known in the Cp series with bridging thiolato[7] and phosphido[8] ligands and are diamagnetic. Therefore, we sought procedures for the preparation of complexes of type **1** which would allow introduction of a

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(1) For part 8 see: Koelle, U.; Raabe, E. *J. Organomet. Chem.* **1985,** *27,* C29.

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(5) Koelle, U.; Fuss, B.; Khouzami, F. *Angew. Chem., Int. Ed. Engl.* **1982,** *21,* 131; *Angew. Chem. Suppl.* **1982,** 230–240.

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broader variety of bridging ligands in order to obtain insight into the variation in Co–Co interaction with different bridges. Nucleophilic exchange of the halides in **1a** and **1b** appeared to be a straightforward synthetic route to the desired compounds (eq 3).

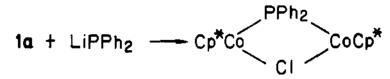
Reaction of **1a** with NaSMe proceeded readily and gave the methanethiolato derivative **1f** in good yield. The analogous reaction with $NaPPh_2$ or $LiPPh_2$ proved more difficult. $(CpCo)_2(\mu\text{-}PPh_2)_2$[8,9] is a known compound, but the product from reaction of **1a** with an excess of $NaPPh_2$ or $LiPPh_2$, after chromatography on alumina, although giving rise to ^1H NMR signals [δ 1.40 (30 H, Cp*), δ ~7.25 (20 H, Ph)] and a mass spectrum [*m/e* (relative intensity) 758 (100, M^+), 379 (10, $M/2^+$)] in agreement with the structure of a bis(diphenylphosphido)-bridged dimer, tended to decompose both in solution and in the solid state and could not be purified to analytical purity.

Reaction of **1a** with $LiPPh_2$ under careful stoichiometric control gave the mixed phosphido/chloro complex **1e** as a stable compound in good yield (eq 4).

$$[Cp^*Co(\mu\text{-}Cl)]_2 + 2MY \longrightarrow [Cp^*Co(\mu\text{-}Y)]_2 + 2MCl \qquad (3)$$

1a

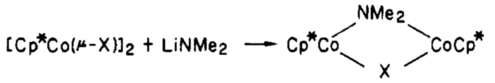
1	f	g	d
MY	NaSMe	TlOEt	NaNH$_2$
Y	SMe	OEt	NH$_2$



$$\mathbf{1a} + LiPPh_2 \longrightarrow Cp^*Co\overset{PPh_2}{\underset{Cl}{\quad\diamond\quad}}CoCp^* \qquad (4)$$

1e

No reaction occurred when **1a** was treated with an excess of NaOEt in THF or pentane. When TlOEt is used, the precipitation of TlCl provides the necessary driving force for the reaction and allows isolation of the ethoxy derivative **1g**. Whereas $NaNH_2$, irrespective of the molar ratio that was used in reaction 3 with either **1a** or **1b**, gave only the amido derivative **1d** (a reaction which is a useful alternative to eq 2), the action of $LiNMe_2$ led to substitution of only one halide ligand in **1a** and **1b** and produced the mixed amido/halo complexes **1h** and **1i**, respectively. The bis(dimethylamido) complex was never obtained. The new complexes were fully characterized by spectral and elemental analyses. Like its Cp analogue, **1f** and notably also **1e** are diamagnetic (by NMR), whereas **1g–i** are paramagnetic and air sensitive, not only in solution, but also as solids.



$$[Cp^*Co(\mu\text{-}X)]_2 + LiNMe_2 \longrightarrow Cp^*Co\overset{NMe_2}{\underset{X}{\quad\diamond\quad}}CoCp^* \qquad (5)$$

1	h	i
X	Cl	Br

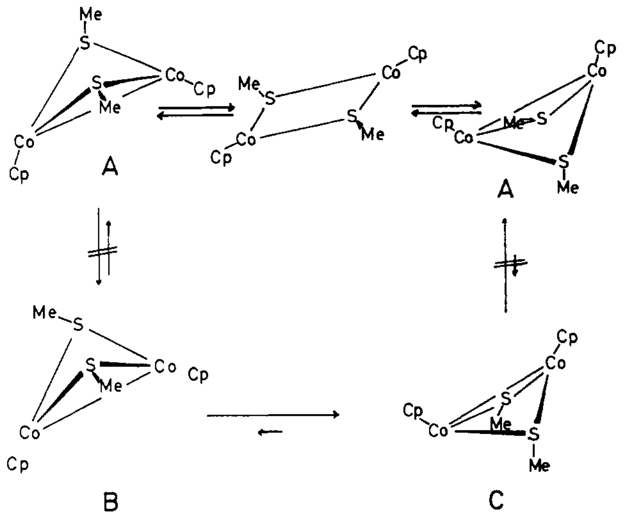
$$[Cp^*Co(\mu\text{-}X)]_2 + 2L \longrightarrow 2Cp^*CoXL \qquad (6)$$

2	a	b	c	d	e
L	py	py	PMe$_3$	PMe$_2$Ph	PMe$_2$Ph
X	Cl	Br	Cl	Cl	Br

Cleavage of the Dinuclear Halo Complexes by Donor Ligands (eq 6). Addition of an excess of pyridine to a pentane solution of **1a** caused immediate precipitation of **2a** as a brown, crystalline solid. A single-crystal structure determination[1] showed the compound to be monomeric in accord with the formulation of the phosphine complexes $CpCoPR_3X$.[2-4]

The bromo complex **1b** also is cleaved by pyridine, but the resulting pyridine adduct **2b** appears to be stable only in the presence of excess pyridine. The situation completely parallels the observations made with analogous Co(III) complexes, $Cp^*CoX_2(py)$,[6] where a stable compound could only be isolated when X was Cl.

Scheme I



Cleavage of the halo bridge by PMe_3 and PMe_2Ph also was analogous to reactions of the Co(III) complexes.[6] In each case Cp*CoX(phosphine) was isolated. The phosphine adducts are much less air sensitive than the pyridine adducts.

Cleavage of **1d**, **1g**, or **1f** with either pyridine or phosphines was sluggish and did not lead to isolable products. The reactions of the halo complexes with a bidentate, chelating ligand, e.g., 2,2′-bipyridine, were similar to those observed with diolefins,[5] in that a valence disproportionation to give Co(I) and Co(III) took place (eq 7). Thus,

$$\underset{\mathbf{1b}}{[Cp^*Co(\mu\text{-}Br)]_2} + 2bpy \longrightarrow$$

$$\underset{\mathbf{3}}{[Cp^*Co(bpy)Br]Br} + \underset{\mathbf{4}}{Cp^*Co(bpy)} \qquad (7a)$$

$$\underset{\mathbf{4}}{Cp^*Co(bpy)} \xrightarrow[\text{2. } NH_4PF_6]{\text{1. } H_2O/O_2} \underset{\mathbf{5}}{[Cp^*Co(H_2O)(bpy)]PF_6} \qquad (7b)$$

addition of an excess of 2,2′-bipyridine to a pentane solution of **1b** caused immediate precipitation of the Co(III) complex **3**, leaving a violet, air-sensitive and thermolabile solution, which contained **4**. Since in this particular case the Co(I) species is not stable,[10] the stoichiometry of eq 7a was established by oxidizing the pentane-soluble Co(I) complex after separation from the Co(III) compound to the previously prepared[6] derivative **5**, precipitated as the hexafluorophosphate from water. The overall yield of **3** and **5** indicated that reaction 7a is essentially quantitative.

Stereodynamic Behavior of $[Cp^*Co(\mu\text{-}SMe)]_2$ (1f). The ^1H NMR spectrum of **1f** exhibits temperature-dependent methyl resonances. A singlet at δ 1.44 (C_6D_6, 80 MHz), observed above 320 K, split into two resonances of equal intensity below 300 K (δ 0.85 and 2.06) representing one methyl group each. From the temperature-dependent line shape, an activation barrier, E_a = 67 kJ/mol ($\Delta H^{\ddagger}_{315}$

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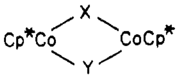
(9) Colman, J. M.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 542.

(10) CpCo(bpy) was previously obtained by the valence disproportionation of CpCoBr at low temperature (Koelle, U., unpublished data) as a dark violet, air-sensitive crystalline solid, characterized by NMR and mass spectrum. It was mentioned recently as the reaction product of $CpCo(C_2H_4)_2$ with bipyridine: Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem. Suppl.* **1983**, 1005–1016. The Cp* derivative appears to be less stable than its Cp analogue. The residue left from evaporation of the pentane solution in reaction 7a gave a mass spectrum in accord with formula **5** but gave neither satisfactory ^1H NMR nor elemental analysis.

Table I. Mass Spectral Data [*m/e* (Relative Intensity)] of Dinuclear Co(II) Complexes



1a–i

no.	X, Y	M^+	$M - X^+$	$M/2^+$ (Cp^*CoX)	$M - 2X^+$ ($[Cp^*Co]_2$, 388) or $M - 2HX^+$ (386)	Cp^*Co (194) or $Cp^*Co{-}H$ (193)
1a	Cl[a]	458 (42)		229 (87)	388	194 (100)
1b	Br[a]	548 (88)		275 (76)		193 (100)
1d	NH_2	420 (100)		210 (15)	386 (80)	193 (100)
1f	SMe	482 (80)	467 (100, $M - Me^+$) 452 (93, $M - 2Me^+$)	241 (16)		
1g	OEt	478 (15)		239 (4)	386 (50)	193 (10)
1h	Cl, NMe_2	467 (27)	422 (50, $M - NHMe_2^+$)	238 (100) Cp^*CoNMe_2	386 (21)	193 (15)
1i	Br, NMe_2	511 (25)	466 (91, $M - NHMe_2^+$)	238 (100)	386 (32)	193 (40)

[a] Fragments containing halogen refer to ^{35}Cl and ^{79}Br, respectively.

= 64.3 kJ/mol, $\Delta S^{\ddagger} \approx 0$), was evaluated. Since splitting is into two methyl signals only and since the pentamethylcyclopentadienyl resonance does not change with temperature, the observed process is assigned to the interconversion of the diastereotopic methyl groups in the syn/anti isomer A as shown in Scheme I.

^1H NMR spectra at 270 MHz in acetone-d_6 exhibit an extra resonance close to the Cp* signal (δ 1.85) in addition to the two coalescing signals, whose line width and intensity are not temperature dependent. This signal can be tentatively assigned to the syn/syn form B. If so, the same molecular motion that equilibrates the diastereotopic methyl groups of the syn/anti isomer would transform the syn/syn form into the anti/anti form C which is disfavored in the equilibrium. The fact that the syn/syn isomer does not participate in the exchange process further argues in favor of an inversion at cobalt rather than at sulfur as the source of the observed equilibration. The limited thermal stability of **1f** and its tendency to decompose in polar solvents do not allow the barrier to inversion to be reached thermally, a process which should equilibrate all of the stereoisomers.

These findings are at variance with those observed for the Rh congener $[CpRh(\mu\text{-}SPh)]_2$,[11] where two distinct conformers, syn/syn and syn/anti, are isolable and are not thermally equilibrated. As inversion at the sulfur atom generally proceeds with a much higher activation energy,[12] the transition state of the interconversion of the methyl groups in **1f** is suggested to be a planar $\overline{\mathrm{Co{-}S{-}Co{-}S}}$ ring with partial or complete rupture of the Co–Co bond. The obviously much higher barrier in at least the syn/anti isomer of the Rh complex thus reflects the stronger Rh–Rh bond, as compared to the Co–Co bond.

Solid-State Structures.[13a] An X-ray crystallographic study of **1h** was only partially successful. Although the observed bond lengths and angles make chemical sense, the refined temperature factors of the carbon atoms are unusually high, in particular for the methyl carbons of the C_5Me_5 ligand. Thus some unresolved disorder is assumed. The shape of the molecule as depicted in Figure 1 is of the familiar butterfly type with Co–Co = 2.49 Å, Co–N = 1.90 Å, and Co–Cl = 2.26 Å, the latter two values in close agreement with those found for the mononuclear pyridine adduct **2a**.[1] The dihedral angle between the planes Co–Co–N and Co–Co–Cl is 117°.

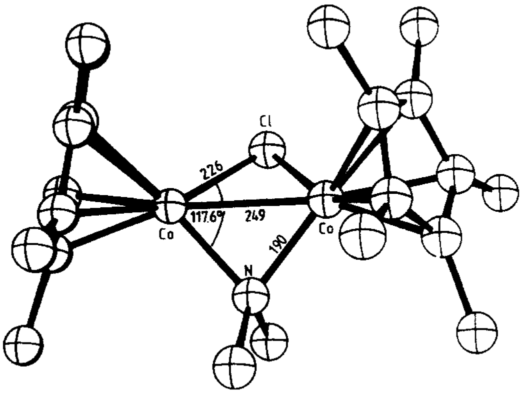


Figure 1. ORTEP representation of $Cp^*Co(\mu\text{-}NMe_2)(\mu\text{-}Cl)CoCp^*$ (**1h**) (bond lengths in pm; hydrogen atoms omitted).

Preliminary structural parameters of **1b**[13b] reveal a basically identical molecular geometry with Co–Co = 2.77 Å and Co–Br = 2.37 Å and a folding angle between the Co–Co–Br planes of 123°.

Mass, EPR, and ^1H NMR Spectra. Prominent fragments in the mass spectra of complexes **1** are collected in Table I, which serves to make apparent the similarities in fragmentation within the series. In each case the molecular ion of the dimer is of high intensity, and only the halo complexes give rise to a prominent peak due to the monomer as well. Besides splitting into monomers, the loss of HX (i.e., NH_3, NMe_2H, or EtOH) is the preferred process. Since no higher mass peaks, indicative of possible polymers, are apparent in the mass spectra, we conclude that a dimeric structure obtains in the gaseous state and for the solids in all cases.

A somewhat more involved picture is necessary to interpret the EPR spectra recorded in frozen solution between 3.6 and 77 K (Table II and parts a and b of Figure 2). The similarity of the two spectra of parts a (**1a**) and b (**2a**) of Figure 2 is immediate proof that the spectrum generated from **1a** is due to a mononuclear Co(II) complex. Apart from slight variations in *g* and *A* values within the series, all the EPR spectra are basically of the same type, i.e., a rhombic **g** tensor with the three components split into octets due to hyperfine coupling to one single Co (*I*

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(11) Connelly, G. N.; Johnson, G. A.; Kelly, B. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1977**, 436.

(12) See: Jesson, J. P.; Muetterties, E. L. In "Dynamic Nuclear Magnetic Resonance"; Jackman, L. M., Cotton, F. A., Eds.; New York, 1975; p 265.

(13) (a) Crystals of **1h** were grown from pentane solution and sealed under argon. From the systematic absences the space group could be either *Pnma* or *Pn*2_1*a*. *Pnma* was chosen for refinement since there were very few observed reflections. Cell constants are *a* = 15.284 Å, *b* = 19.054 Å, and *c* = 7.812 Å for *Z* = 4. Final *R* value was 0.047 for 120 variables and 367 reflections. (b) Koelle, U.; Hessner, B., to be submitted for publication.

Table II. EPR Spectral Parameters for Complexes 1 and 2 in Frozen Solutions

no.	solv	T, K	g_z	g_y	g_x	A_z, G	A_y, G	A_x, G
1a[a]	THF	54	2.287	1.972	2.095	96.0	14.0	38.0
1a[a]	toluene	55	2.287	1.955	2.077	96.6	16.0	38.5
1a[a]	3-methylpentane	48	2.31	1.97	2.08	82.5	*b*	*b*
1a[a]	powdered solid	21	2.32		2.07	94	*b*	*b*
1d	3-methylpentane	32	2.25		2.06	81	*b*	*b*
1g	THF	10	2.21	1.97		100	*b*	42
2a[a]	THF	54	2.290	1.97	2.079	80.0	16.0	30.0
2c[c]	toluene	77	2.29	1.97	2.06	73	20	30

[a] Parameters extracted from computer-simulated spectra. [b] Hyperfine splitting not resolved. [c] A_z(Co–P) = 18.6 G.

Table III. Proportion of the Monomeric Complex Cp*CoClS in Different Solvents (S) from Integrated EPR Intensities

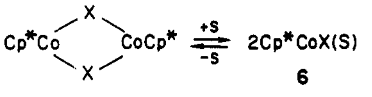
solv	% monomer	T, K
none	0.25	4
pentane	6	4
toluene	8	54
THF	33	55
pyridine	100	54

Table IV. ^{1}H NMR Absorptions (δ) of Complexes 1 and 3 in Solution

no.	solv	Cp*	other signals
1a	toluene-d_8	38.5[a]	
1a	cyclohexane-d_{12}	41	
1d	toluene-d_8	2.4	−2.9 (NH_2)
1g	cyclohexane-d_{12}	50.5	28.0 (CH_2), −5.0 (CH_3)
1h	cyclohexane-d_{12}	42	3.3 (CH_3)
2a	toluene-d_8	none	8.4, 4.6 (pyridine)

[a] Shifts refer to internal Me_4Si of a diamagnetic solution, measured by setting the appropriate internal reference frequency of the deuterium lock signal.

= $^7/_2$) nucleus. (Since the coupling parameter in the dimer is $J \simeq 200$ cm^{-1} (see below) and the hyperfine coupling constant is $A \simeq 80$ G $\simeq 0.75 \times 10^{-2}$ cm^{-1} (Table II), the condition $J >> A$ holds and should give rise to a 15-line pattern in the spectrum of the dimer.) A solvent-dependent monomer/dimer equilibrium (eq 8), where EPR



1 6 (8)

S = solvent

monitors only the monomer, is consistent with these observations. Quantitative experiments revealed drastic variations in EPR signal intensity with solvent for **1a** but not for, e.g., **1g**, which produced low intensity signals in hydrocarbon as well as in donor solvents. With use of the pyridine adduct **2a** as a standard (see Experimental Section), the proportion of monomer in different solvents and in the solid was evaluated (Table III). As expected, the data in Table III show a shift toward the monomer with increasing donor capacity of the solvent. The very low intensity produced by the powdered solid may then be due to surface imperfections.

The existence of the dimeric complexes in solution, on the other hand, is demonstrated from solution ^{1}H NMR spectra (Table IV). A broad signal ($\Delta\nu$ = 300–1000 Hz), 40–50 ppm downfield from Me_4Si, typical of the absorption of methyl protons on a Cp* ligand in Co(II) sandwhich complexes,[14] was observed. A noteworthy, yet unexplained exception, is the amido complex **1d** whose rather sharp methyl absorption appears in the diamagnetic shift region.

Table V. Effective Magnetic Moments (μ_B) of Complexes 1 and 2a at Two Different Temperatures[a]

no.	μ_{eff}(298 K)	μ_{eff}(20 K)
1a	1.19	0.48
1d	1.04	0.58
1g	2.60	2.70
1i	0.71	0.43
1h	0.68	0.48
2a	1.91	1.91

[a] Values are calculated from χ_{mol} under the assumption of negligible θ (see text) and are referred to one Co to allow for direct comparison of complexes 1 with **2a**.

Spectra of **1a** in toluene-d_8 (entry 1 in Table IV) were followed over the temperature range 170–333 K where the chemical shift of the Cp* signal, though broadened at lower temperature, remains virtually constant. The lack of an inverse temperature-dependent chemical shift, generally characteristic of simple paramagnetic molecules,[15] can be accounted for if the observed signals are due to dimeric molecules with a temperature-dependent, intramolecular coupling. In fact, if a coupling parameter, J = 240 cm^{-1} (see below), is introduced into the expression $\delta \propto 1/T(1 + \exp(J/kT))$ describing the variation of paramagnetic chemical shift associated with a temperature-dependent equilibrium, a shallow maximum below the detection level is obtained in the temperature range in question. Analogous behavior was recently demonstrated with structurally related dimeric $CpCrX_2$ complexes.[16] In contrast, no signal due to the Cp* ligand in **2a** could be detected. Instead, pyridine, added in increasing proportions to a toluene solution of **1a**, caused successive broadening and finally complete disappearance of the low field Cp* signal.

Solid-State Magnetism. Solid-state susceptibilities of powdered samples of **1a**, **1d**, **1g**, **1h**, **1i**, and **2a** were measured in the temperature range 4–290 K on a Faraday balance.[17] Plots of $1/\chi$ vs. T are shown in Figure 3. The mononuclear complex **2a**, serving as the reference compound, exhibits perfect Curie behavior with a Θ of O K within experimental error, which means that intermolecular interaction of unpaired spins in the crystal lattice of these organometallic complexes is small. The effective magnetic moment of **2a** (Table V) is somewhat in excess of the spin-only value for one unpaired electron, indicating some orbital contribution.

For the dimeric complexes the susceptibility at low temperature (<50 K) is largely determined by the paramagnetic impurities always present in small proportions. At higher temperature large deviations from a Curie–Weiss straight line plot indicate that the susceptibility in this temperature region is dominated by magnetic interaction within the dimers.

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[14] Koelle, U.; Fuss, B.; Ramakrishna, B. L.; Rajasekharan,M. V.; Ammeter, J. H.; Boehm, M. C. *J. Am. Chem. Soc.* **1984**, *106*, 4152.

[15] Jesson, J. P. In "NMR of Paramagnetic Molcules"; LaMar, G. N., Horrocks, W. DeW., Holm, R. H. Eds.; New York, 1973; p 9 ff.

[16] Köhler, F. H.; deCao,R.; Ackermann, K.; Sedlmaier, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1406.

[17] Lueken, H.; Rohne, W. *Z. Allg. Anorg. Chem.* **1975**, *418*, 103.

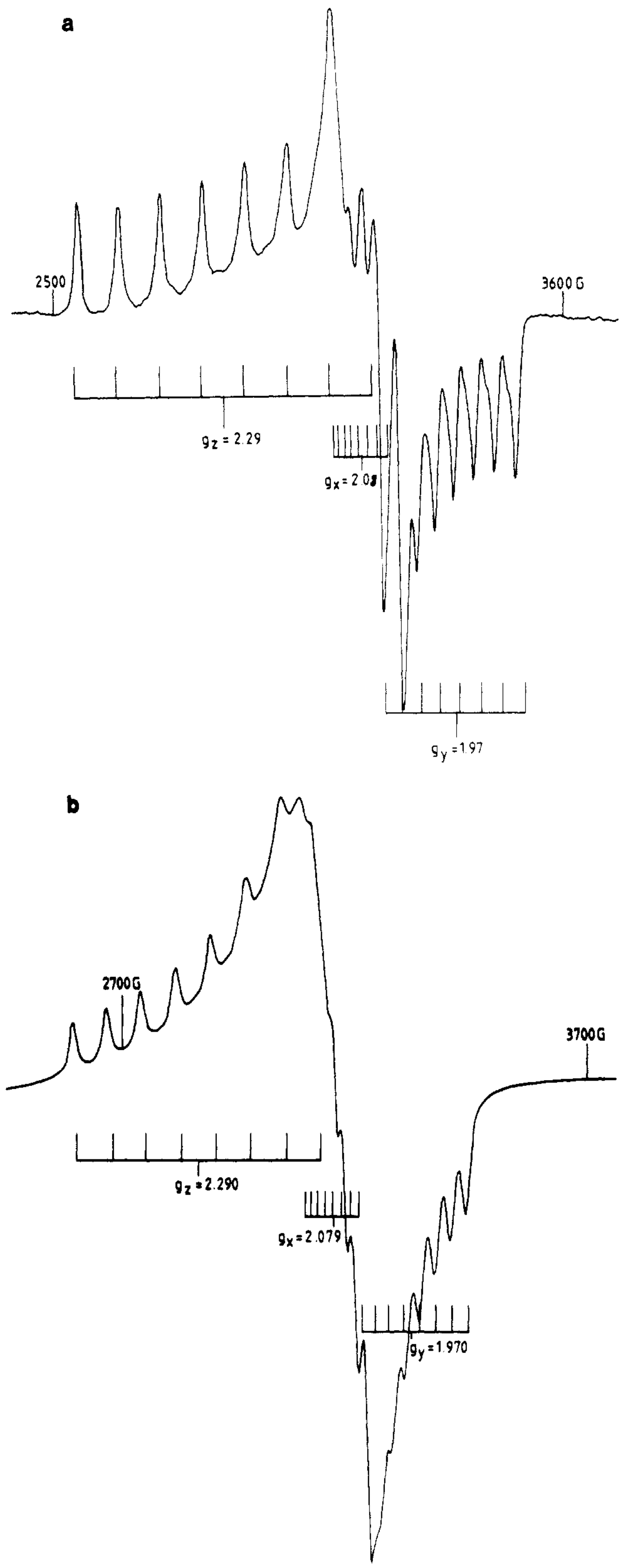


Figure 2. (a) EPR spectrum of $[Cp^*CoCl]_2$ (**1a**), in toluene at 55 K (ν = 9187 MHz). (b) EPR spectrum of $Cp^*Co(py)Cl$ (**2a**), in THF at 54 K (ν = 9186 MHz).

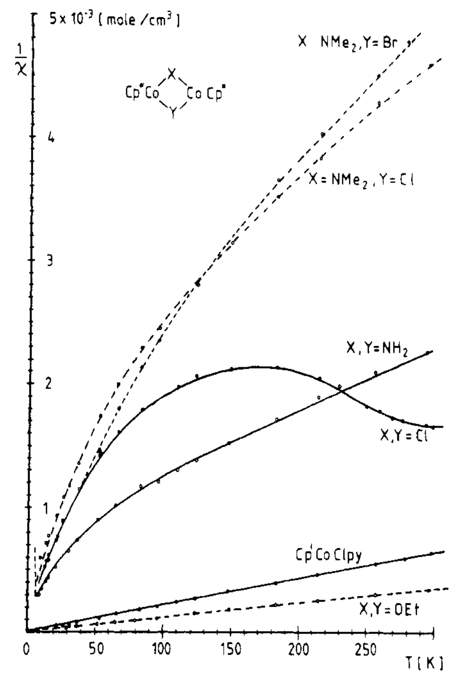


Figure 3. Inverse susceptibilities $1/\chi_{mol}$ vs. temperature for complexes **1** and **2a**.

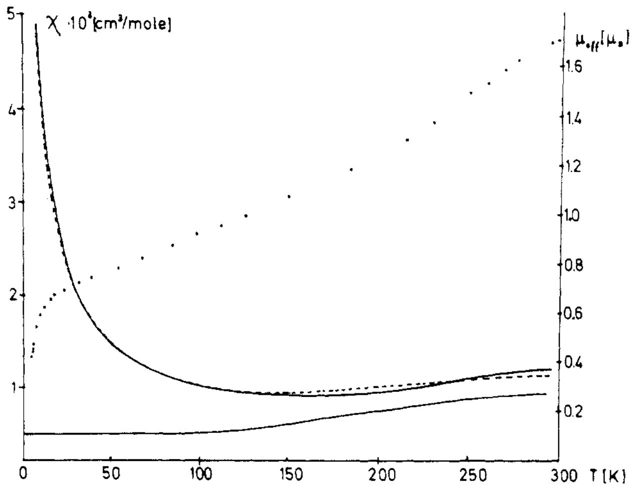


Figure 4. Observed (—) and calculated (- - -) molar susceptibility vs. temperature of **1a**. The lower curve represents χ_{mol} vs. T calculated without paramagnetic contribution. Coupling parameter for the calculation is J = -238 cm^{-1}; effective magnetic moment μ_{eff} calculated under the assumpton of zero Θ. Both parameters refer to the dimeric formula unit $[Cp^*CoCl]_2$.

In all cases, except **1g**, were χ_{mol}/Co exceeds the value found for **3a**, the dimeric complexes showed susceptibilities considerably reduced from the spin value and temperature-dependent effective magnetic moments (Table V), calculated from χ_{mol} under the assumption of a zero Θ at low temperature. The solid-state magnetic behavior thus indicates an antiferromagnetic interaction between the two d^7 centers increasing in the ligand order halo < amido < halo/dimethylamido. In **1g**, in contrast, the Co centers appear to be ferromagnetically coupled.

The weakest coupling is observed in **1a**, where the $1/\chi$ vs. T plot exhibits the largest curvature in the accessible temperature range, which means that the singlet/triplet equilibrium within the dimer largely dictates the overall susceptibility down to at least 150 K. An effort to simulate the $1/\chi$ vs. T curve for **1a** gave the best fit of the calculated to the experimental susceptibility (Figure 4) with a coupling parameter of J = -238 cm^{-1}. This rather strong coupling offers a ready explanation for the fact that no EPR spectra due to dimers were observed. Because of two closely spaced Kramer's doublets in most d^7 sandwich and half-sandwich complexes, an efficient relaxation mechanism is provided and the observation of EPR spectra is generally confined to low temperatures. At these temperatures, by virtue of the strong antiferromagnetic coupling in complexes **1**, the singlet/triplet equilibrium lies entirely toward the singlet. In fact, in those cases, in which

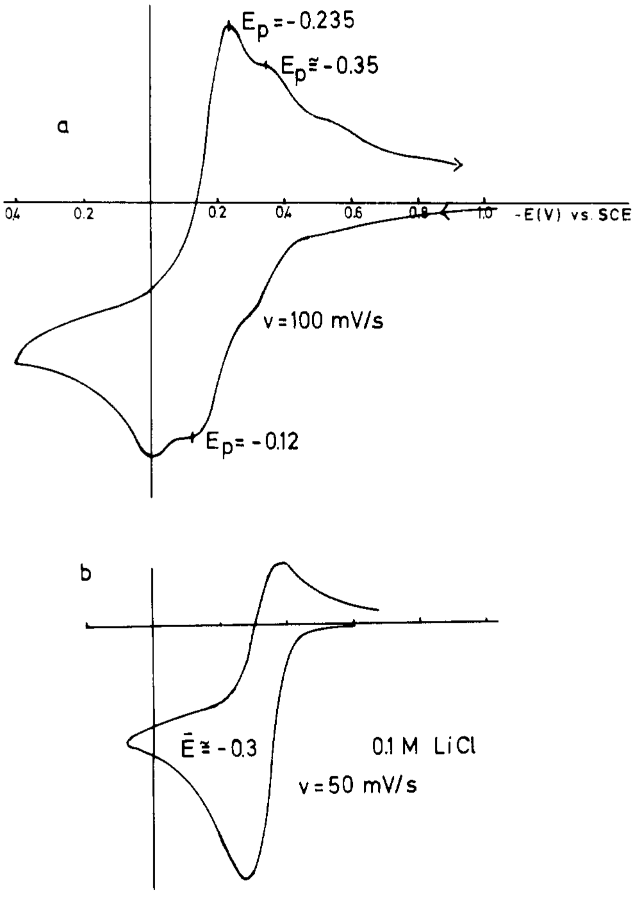


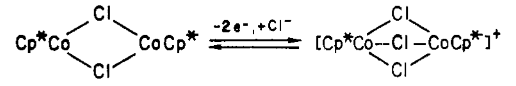
Figure 5. (a) Cyclic voltammogram of **1a** (10^{-3} M) in THF/TBAH at a Pt electrode (scan rate v = 100 mV/s). (b) As before with 0.1 M LiCl added (v = 50 mV/s).

EPR spectra of magnetically coupled dimers were observed, the coupling does not exceed a few reciprocal centimeters.[18]

Redox Behavior. In view of the extreme air sensitivity, in particular of complexes **1a–1d**, it was anticipated that these may be strong reducing agents, similar to cobaltocene[19] or its permethyl derivative.[20] Polarographic and cyclic voltammetric investigation of **1a** and **1d** did not substantiate this expectation.

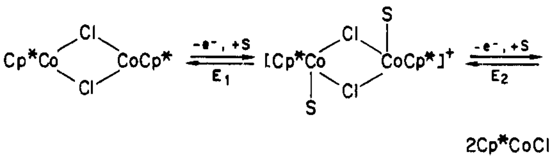
Complex **1a** in THF shows a polarographic oxidation wave at $E_{1/2}$ = –0.25 V vs. SCE, which is composed of at least two individual waves. From the cyclic voltammogram (Pt electrode) of the compound with tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte (Figure 5a) oxidation of three different species, tentatively assigned to the monomer and the dimer (see below), is detectable.

Addition of LiCl causes a color change from brown to blue and greatly simplifies the cyclic voltammogram (Figure 5b), leaving a single reversible peak at about the same potential. Recalling that chemical oxidation of complexes **1** proceeds with incorporation of one additional anionic ligand to give a dinuclear Co(III)–Co(III) complex, $7^{5,6}$ (eq 9), the lack of such a ligand in the absence of excess chloride may cause the dimer to be oxidized in two distinct steps at E_1 and E_2 (eq 10), which, along with a step for the monomeric THF adduct (eq 11), can account for the three waves in Figure 5a. An excess of chloride could generate a chloro complex, **8**,[21] in which the oxidation and dimerization to produce again **7** (eq 12) appear as a single reversible wave in the cyclic voltammogram, provided exchange of the chloride is fast on the electrochemical time scale.



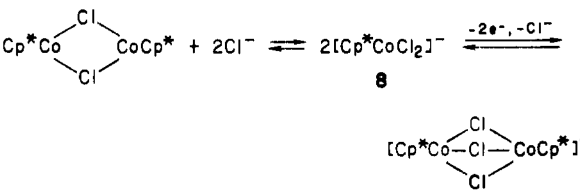
(9)

$7^{4,5}$



(10)

$$Cp^*CoCl(S) \xrightarrow[E_3]{-e^-,\ +S} Cp^*CoCl(S)_2^+ \quad (11)$$



(12)

Complex **1d** under similar conditions (THF/TBAH) in the polarogram and in the cyclic voltammogram (hanging Hg drop) showed an irreversible oxidation wave at $E_{1/2}$ = –0.6 V vs. SCE assigned to the formation of one or several Co(III) species. Admission of air gives a mauve-colored solution and causes this wave to disappear while a new irreversible reduction wave is generated near –1 V. After having swept through this wave, the original oxidation wave at –0.6 V reappears which means that the starting material is regenerated on reduction of the oxygenated complex.

These observations suggest that air oxidation may involve oxygen uptake rather than electron transfer, a feature common to many classical Co(II) coordination compounds. In line with this interpretation is the puzzling fact that complexes **1**, despite their extreme air sensitivity, are not really strong reducing agents in an electron-transfer sense as seen by their oxidation potentials which are not at all extremely negative.

Discussion

The preparation of the complexes described above establishes a half-sandwich chemistry of Co(II) with ligands ranging from rather hard (Cl) to quite soft (PR_2). Counting valence electrons, the monomeric and the paramagnetic dimeric complexes all have a 17-electron valence shell. Addition of donor ligands to the dimers with hard bridging ligands effects bridge cleavage; thus a 19-electron complex appears to be unfavorable as it is the case in classical coordination compounds of Co(II).

The intriguing feature of the dimeric complexes is, of course, the varying degree of electron coupling with the nature of the bridging ligands. Obviously, this coupling is weakest with σ-donor ligands like chloride, e.g., **1a**, and strongest if the bridging atoms have acceptor properties as in **1e** and **1f**, the amido complexes being intermediates. The situation is reminiscent of structurally related nickel allyl complexes $(\eta^3\text{-}C_3R_5)Ni(\mu\text{-}X)_2Ni(\eta^3\text{-}C_3R_5)$, where a

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[18] (a) Francesconi, L. C.; Corbin,D. R.; Clauss, A. W.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1981**, *20*, 2059. *Ibid.* 1981, *20*, 2070. (c) *Ibid.* **1981**, *20*, 2078. (d) *Ibid.* **1981**, *20*, 2084.

[19] Gubin, S. P.; Smirnova, S. A.; Denisovich, L. I. *J. Organomet. Chem.* **1971**, *30*, 257.

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[21] The frozen solution EPR spectrum of the blue chloride adduct was of the same type as the other monomer spectra and was of high intensity, in agreement with a mononuclear anionic dichloro species.

conformational change from a planar $\overline{\text{Ni–X–Ni–X}}$ rhomboid to a folded (butterfly) conformation with concomitant shortening of the Ni–Ni distance occurs when the bridging ligands are altered from X = Br or MeO (Ni–Ni = 3.24 Å[22]) to X = SMe (Ni–Ni = 2.75 Å[23]) or Me (Ni–Ni = 2.37 Å[23]).

The limited amount of structural data at hand (neither **1a** nor **1f** despite repeated attempts gave crystals of X-ray quality) suggests that a similar relation exists between the Co–Co distance and the bridging groups also in the present case though the change in the dihedral angle between Co–X–Co planes in **1b** (123.5°) and **1h** (117.6°) appears to be marginal. Comparison of the Co–Co bond lengths in paramagnetic **1b** (2.77 Å) and **1h** (2.49 Å) with the value of 2.56 Å determined for $(CpCo)_2(\mu\text{-}PPh_2)$ (**9**)[24] and related phosphido-bridged derivatives, all of which are diamagnetic and are formulated with a Co–Co bond, indictes that for magnetic coupling the metal–metal distance is not the only parameter of importance.

The molecular orbital picture presented by Burdett[25] for the closely related and isoelectronic series $(Fe(CO)_3)_2(\mu\text{-}ER_2)_2$ (E = N, P, As), and similar arguments given by Pinhas and Hoffmann[26] may be used to give an explanation on electronic rather than on mere structural grounds.

Thus, the lower (bonding) degenerate pair of e levels of a $L_nM\text{–}ML_n$ fragment of C_{nv} symmetry, which is derived from the $e_1{}^*$ levels of the individual L_nM fragments, is doubly occupied in case this has a d^7 electron configuration. These levels are split into a_1 and b_2 by lowering the symmetry to C_{2v} or C_s, i.e., by combining the L_nM fragments via bridging ligands in a planar or puckered mode, respectively. As shown by the MO calculations,[25,26] the lifting of the degeneracy of the HOMOs is largely due to interaction with an acceptor ligand in the bridge and in general parallels the amount of puckering (folding around the E–E axis). The dihedral angles between the P–Co–P planes in **9**, 105°, and the Cl–Co–N planes in **1h**, 107°, are nearly identical, which should lead to about equal splitting of the a_1/b_2 levels in both complexes. On the other hand, a dihedral angle smaller than about 105° in the Cp* complexes may be unfavorable because the Cp* methyl groups come to closely approach. This may also be the reason for the obvious instability of the PPh_2-bridged complex in the Cp* series. If the degree of puckering is then fixed by geometric constraints, level splitting, directly related to the singlet–triplet energy difference, only depends on the donor/acceptor properties of the bridging ligands. Since the singlet–triplet energy difference is of the order 3×10^{-3} eV in **1a** and is higher in the dimethylamido complexes, minor changes in the acceptor properties of the bridging ligands are necessary to shift the spin equilibrium to either side. Obviously the halo and amido complexes are just at the limit of beginning bond formation between the Co atoms.

Experimental Section

All mainpulations were carried out under a nitrogen atmosphere with anhydrous solvents which were saturated with nitrogen. Glassware was heated under vacuum prior to use. Cp*Li was prepared as described in ref 6a. ^{1}H NMR spectra were recorded on Bruker WH 270 and SY 80 instruments at 270 and 80 MHz. X-band EPR spectra were measured on a Bruker ER 420 spectrometer equipped with an NMR gaussmeter.

Bis[(μ-chloro)(pentamethylcyclopentadienyl)cobalt] (1a). Anhydrous $CoCl_2$ (1.32 g, 11 mmol) and Cp*Li (1.42 g, 10 mmol) were stirred in 20 mL of THF for 10–20 min at ambient temperature. The solvent was removed in vacuo to leave a dark brown solid or oily residue (complete removal of the solvent is not advisable since the product can be extracted only with difficulty from the completely dried reaction mixture). This was extracted with three 100-mL portions of pentane. The combined pentane extracts were filtered and concentrated to about 100 mL. Cooling to −70 °C precipitated the product as brown-black microcrystals. It can be sublimed at 100 °C (10^{-3} torr) with some decomposition; yield 2.26 g (90%). See ref 5 for analysis.

Bis[(μ-bromo)pentamethylcyclopentadienyl)cobalt] (1b) was prepared analogously to **1a** with a molar amount of $CoBr_2\cdot DME$; yield 80%. See ref 5 for analysis.

Bis[(μ-amido)(pentamethylcyclopentadienyl)cobalt] (1d). The suspension from 3.35 g (10 mmol) of $Co(NH_3)_6(BF_4)_2$[27] and 1.42 g (10 mmol) of Cp*Li in 40 mL of THF was stirred at 40 °C for 3 h while the mixture gradually turned green. The solvent was evaporated and the green, oily residue extracted with 100 mL of pentane. After filtration, the pentane extract was concentrated to about 20 mL. On being cooled to −80 °C, the product crystallized as green needles. The mother liquor was removed with a syringe and the solid dried under vacuum at dry ice temperature. **1d** appears to be the most air sensitive of the Co(II) complexes described herein. On exposure to air it immediately turns violet and becomes insoluble in pentane. Anal. Calcd for $C_{20}H_{34}Co_2N_2$ (416.3): C, 57.15; H, 8.15; N, 6.88. Found C, 56.88; H, 8.04; N, 6.80.

Bis[(μ-ethoxy)(pentamethylcyclopentadienyl)cobalt] (1g). To a solution of 2.3 g (5 mmol) of **1a** in 30 mL of pentane was added 2.5 g (10 mmol) of TlOEt. The solution was filtered from the TlCl which separated instantaneously. The filtrate was concentrated to a small volume and the product crystallized on cooling to −80 °C; yield 2.2 g (92%). Anal. Calcd for $C_{24}H_{40}Co_2O_2$ (478.4): C, 60.29; H, 8.37. Found: C, 60.44; H, 8.22.

Bis[(μ-methanethiolato)(pentamethylcyclopentadienyl)cobalt] (1f). A mixture of 0.47 g (1.6 mmol) of **1a** and 1 g (14 mmol) of NaSMe in 50 mL of THF was stirred for 12 h at ambient temperature. The solvent was evaporated, the residue extracted with pentane, and the pentane solution filtered and cooled to −80 °C to give 0.55 g (70%) of green crystals, mp 250 °C dec. Another 100 mg crystallized from the concentrated mother liquors. Anal. Calcd for $C_{22}H_{36}Co_2S_2$ (482.5): C, 69.67; H, 7.04. Found: C, 69.45; H, 6.72.

(μ-Chloro)(μ-diphenylphoshido)bis[(pentamethylcyclopentadienyl)cobalt] (1e). To 2.3 g (5 mmol) of **1a** in 20 mL of THF was added 2.3 g (11 mmol) of $LiPPh_2$,[28] and the mixture was stirred for 1 h at ambient temperature. After removal of the solvent, extraction with pentane, filtering, and cooling to −80 °C, 2.0 g (74%) of black crystals separated: mp 215–220 °C, ^{1}H NMR (CD_2Cl_2) δ 1.50 (s, 30 H, Cp*), ~7.25 (m, 10 H, Ph); mass spectrum, *m/e* (relative intensity) 608 (M^+, 35), 379 (Cp^*CoPPh_2, 100), 278 ($CoClPPh_2$ H, 93). Anal. Calcd for $C_{32}H_{40}ClCo_2P$ (608.9): C, 63.11; H, 6.62. Found: C, 63.36; H, 6.82.

(μ-Chloro)(μ-dimethylamido)bis[(pentamethylcyclopentadienyl)cobalt] (1h). A pentane solution of **1a** (2.2 g, 4.4 mmol) was stirred with 0.25 g (10 mmol) of $LiNMe_2$ for 3 h at ambient temperature. The solution was filtered, concentrated, and cooled to yield 1.5 g of dark brown-violet crystals: yield 60%; mp 200 °C dec. Anal. Calcd for $C_{22}H_{36}ClCo_2N$ (467.9): C, 56.45; H, 7.76. Found: C, 56.34; H, 7.56.

(μ-Bromo)(μ-dimethylamido)bis[(pentamethylcyclopentadienyl)cobalt] (1i) was prepared as described for **1h** from **1b** and $LiNMe_2$: yield 71%; mp 200 °C dec. Anal. Calcd for $C_{22}H_{26}BrCo_2N$ (513.3): C, 51.58; H, 7.08. Found: C, 51.32; H, 6.95.

Chloro(pentamethylcyclopentadienyl)(trimethylphosphine)cobalt (2c). To a solution of 1 g (2.2 mmol) of **1a** in 20 mL of pentane was added 0.38 g (5 mmol) of trimethylphosphine. The solution turned violet; it was filtered and cooled to −80 °C when the product separated as red crystals: yield 1.26

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g (95%); mass spectrum [*m*/*e* (relative intensity) with ref to ^{35}Cl] 305 (M$^+$, 21), 194 (Cp*Co$^+$, 50), 135 (Cp*, 33), 76 (PMe$_3$, 100). Anal. Calcd for $C_{13}H_{24}ClCoP$ (304.7): C, 51.08; H, 7.91. Found: C, 50.94; H, 7.88.

Chloro(pentamethylcyclopentadienyl)(dimethylphenylphosphine)cobalt (2d) was prepared analogously to **3c** from 1.0 g (2.2 mmol) of **1a** and 0.69 g (5 mmol) of dimethylphenylphosphine: yield 1.45 g (90%); mass spectrum, *m*/*e* (relative intensity) 367 (M$^+$, 16), 229 (M − PPhMe$_2$$^+$, 100), 194 (Cp*Co$^+$, 52). Anal. Calcd for $C_{18}H_{26}ClCoP$ (367.8): C, 58.79; H, 7.08. Found: C, 58.78; H, 7.05.

Bromo(pentamethylcyclopentadienyl)(dimethylphenylphosphine)cobalt (2e) was prepared analogously to **3c** from **1b** and dimethylphenylphosphine: yield 1.4 g (85%); mass spectrum, *m*/*e* (relative intensity) 411 (M$^+$, 13), 332 (M − Br$^+$, 40), 274 (M − PPhMe$_2$$^+$, 57), 194 (Cp*Co$^+$, 37). Anal. Calcd for $C_{18}H_{26}BrCoP$ (412.2): C, 52.45; H, 6.36. Found: C, 52.12; H, 6.12.

Determination of EPR Intensities of 1a in Different Solvents. Equal portions (0.1 mL) of solutions containing 20 mg/mL of **1a** in pentane, toluene, or THF were transferred by syringe under nitrogen into two EPR quartz sample tubes. To one sample was added 0.1 mL of the respective solvent and to the other one were added the solvent (toluene for the case of the pentane solution to ensure dissolution at room temperature) and excess pyridine to make a total of 0.2 mL in either tube. The samples were shock frozen in liquid nitrogen and measured at the temperatures indicated in Table III.

Acknowledgment. This work was supported by the "Deutsche Forschungsgemeinschaft" and by the "Fonds der Chemischen Industrie". We are indebted to Dr. H. Leuken and his co-workers from this Institute for the susceptibility measurements and the simulation of the χ vs. *T* curve. Drs. H. Twilfer and A. Raap, Institute of Physiological Chemistry, Technical University Aachen, are thanked for help with the EPR spectroscopy. We further thank Dr. B. L. Ramakrishna, Washington State University, Pullman, WA, for simulating some of the ESR spectra.

Registry No. **1a**, 74353-89-2; **1b**, 82595-79-7; **1d**, 82595-81-1; **1e**, 100928-27-6; **1f**, 100928-28-7; **1g**, 100928-29-8; **1h**, 100928-30-1; **1i**, 100928-31-2; **2c**, 100928-32-3; **2d**, 100928-33-4; **2e**, 100928-34-5; $Co(NH_3)_6(BF_4)_2$, 13877-19-5; $CoCl_2$, 7646-79-9; Cp*Li, 51905-34-1; $CoBr_2$, 7789-43-7; Co, 7440-48-4.

Kinetics and Mechanism of the Reaction of [Et$_4$N][HFe(CO)$_4$] and Alkyl Halides. The Unexpected Formation of Acetone

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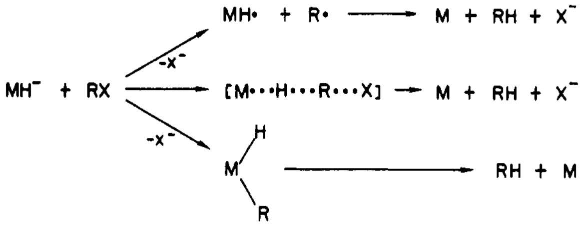
When [Et$_4$N][HFe(CO)$_4$] is treated with methyl iodide in CH_3CN at 25.0 ± 0.2 °C, a clean second-order reaction ensues as monitored via the change in the intensity of ν_{CO} of the metal carbonyl hydride. In all cases, yields of CH_4 were 85–100%. A second-order rate constant (first order in iron and in CH_3I) of $(1.7 \pm 0.1) \times 10^{-2}$ M^{-1} s^{-1} was determined, and activation parameters of $E_a = 11.2 \pm 1.0$ kcal/mol, $\Delta H^{\ddagger} = 10.6 \pm 1.0$ kcal/mol, and $\Delta S^{\ddagger} = -33$ cal/(mol K) were found over the temperature range 15–35 °C. The iron product from this reaction is thought to be the unstable "Fe(CO)$_4$(NCCH$_3$)", which can also be generated from Fe(CO)$_5$ in CH_3CN by irradiation or use of $(CH_3)_3NO$. Reaction of iron hydride with 6-bromo-1-hexene produced only 1-hexene and no detectable methylcyclopentane. Reaction with cyclopropylcarbinyl bromide yielded primarily methylcyclopropane and lesser amounts of 1-butene and *cis*- and *trans*-2-butene, although evidence is presented to suggest nonrigorously that this is a side reaction. A simple nucleophilic substitution is proposed as the rate-determining step. During this study acetone was detected and confirmed as a reaction product by isotope-labeling studies. A mechanism for this latter observation is discussed.

Introduction

Transition-metal hydride anions can dehalogenate organic halides RX to RH through a variety of pathways. Among those available are electron transfer (SET) and nucleophilic displacement. Nucleophilic displacement reactions may occur via attack on the carbon atom by (1) the metal center (followed by reductive elimination) or by (2) the hydride ligand.

Scheme I



Kinney, Jones, and Bergman, in studying [CpV(CO)$_3$H]$^-$, saw evidence for both SET- and S$_N$2-type reactions depending on the organic substrate being dehalogenated.[1] M. Y. Darensbourg and co-workers have recently examined the group VI (6[24]) metal hydride anions [HM(CO)$_4$L]$^-$ (M = Cr, Mo; L = CO, PR$_3$) as well as [HFe(CO)$_3$L]$^-$ (L = CO, PR$_3$) and some related complexes[2,3] and have developed a reactivity scale based on these results. Again, SET or S$_N$2 processes were possibly dependent on the metal complex employed. Darensbourg's work suggested that the reactions of [HFe(CO)$_4$]$^-$ would likely proceed by SET processes.[3] We had begun our study of [HFe(CO)$_4$]$^-$ with alkyl iodides before Darensbourg's initial reports and found

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