spectra. The spectrometer was a Spex Industries Model 14018 double monochromator equipped with 1800-grooves/mm holographic gratings. An RCA C31034 phototube detector in conjunction with a pulse count system consisting of pulse amplifier, analyzer, and rate meter (Hamner NA-11, NC-11, and N-78A, respectively) and a Texas Instruments Model FSOZWBA strip chart recorder were used to record the spectra. The spectrometer was periodically calibrated by recording the discharge lines from an argon lamp over the spectral range of interest; the Raman shifts quoted are estimated to be accurate to ±1 cm^{-1}. Slit widths depended on the scattering efficiency of the sample, laser power, etc., with 1.0 cm^{-1} being typical.

FEP reaction vessels were mounted vertically. The angle between the incident laser beam and the sample tube was 45°, and Raman scattered radiation was observed at 45° to the laser beam (90° to the sample tube axis).

All spectra were recorded at −196 °C by mounting the sample vertically in an unsilvered Pyrex glass Dewar filled with liquid nitrogen.

Acknowledgment. We thank the Science and Engineering Research Council of Great Britain (J.H.H.) and the Natural Sciences and Engineering Research Council of Canada (G.J.S.) for financial support of this work, NATO for travel grants (D.M.-R. and G.J.S.), and the University of Leicester Computer Laboratory for use of their facilities. H.S. and V.K. were on leave from the Hebrew University of Jerusalem, Israel, and Edvard Kardelj University of Ljubljana, Yugoslavia, respectively. We also thank Prof. Hendrik de Waard, Laboratorium voor Algemene Natuurkunde, University of Groningen, The Netherlands, for obtaining the ^{129}Xe Mössbauer data on $Cs^+[XeOF_5]^-$.

Registry No. $Cs^+[(XeOF_4)_3F]^-$, 76077-76-4; $XeOF_4$, 13774-85-1; $Cs^+[XeOF_5]^-$, 12191-01-4; ^{18}O, 14797-71-8.

Supplementary Material Available: Listings of thermal parameters, observed and calculated structure factors, and details of least-squares planes and Figures 2 and 4 showing a stereoscopic view of the unit cell and a view down the fourfold axis of one $XeOF_4$ group in $Cs^+[(XeOF_4)_3F]^-$, respectively (7 pages). Ordering information is given on any current masthead page.

Contribution from the Institut für Anorganische Chemie, Technische Universität München, D-8046 Garching, West Germany, and Institut für Anorganische Chemie der Rheinisch-Westfälischen Technischen Hochschule Aachen, D-5100 Aachen, West Germany

Antiferromagnetic Coupling of Cobalt (d^9) Centers Mediated by the Norbornadiene π Systems

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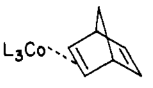
The synthesis and properties of cobalt(0) complexes with bicyclo[2.2.1]heptadiene, $Co(C_7H_8)(PMe_3)_3$ and $C_7H_8[Co(PMe_3)_3]_2$, and with bicyclo[2.2.1]heptene, $Co(C_7H_{10})(PMe_3)_3$, are reported. The X-ray structure investigation of the binuclear exo/exo metal complex with the norbornadiene bridge shows that it crystallizes in the monoclinic space group $C2/c$, with a = 15.743 (4) Å, b = 9.291 (3) Å, c = 28.777 (9) Å, β = 116.94 (2)°, and Z = 4. The structure shows isolated molecular units with each cobalt tetrahedrally surrounded by three phosphane ligands and one olefinic function. From magnetic susceptibility data, a remarkably strong antiferromagnetic coupling of the d^9 centers (d_{Co-Co} = 5.749 (1) Å) involving through-space interactions between the norbornadiene π systems is found (singlet–triplet splitting $\Delta E = E(T) - E(S) \approx 500\ cm^{-1}$).

Introduction

Zerovalent cobalt forms mononuclear complexes of composition $Co(olefin)(PMe_3)_3$.[1-3] Complexes of $Co(olefin)_2(PMe_3)_2$ can be synthesized by using diolefin ligands with isolated double bonds, provided chelating effects enhance the thermal stability of such systems.[3] We found bicyclo[2.2.1]heptadiene reacting with cobalt(0) centers not in this fashion but forming mono-exo and bis-exo complexes **1** and **2**.



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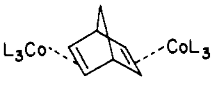

2

There has been considerable interest in π-orbital interactions in oligocyclic unsaturated molecules.[4-6] Serving as ligands for two or more paramagnetic metal centers, these molecules are expected to transmit unpaired electron density, thereby mediating spin–spin coupling between valence shells of metal centers. We therefore set out to determine the crystal structure and to investigate the magnetic properties of complex **2**.

Experimental Section

Methods and Analyses. Standard high-vacuum techniques were used in handling volatile and air-sensitive material.[7] Combustion analyses were carried out by W. Barth, U. Graf, and G. Schuller in the Garching microanalytical laboratory. Trimethylphosphine was prepared from triphenyl phosphite and methylmagnesium chloride.[8] Norbornadiene (reagent grade; Merck-Schuchardt) was distilled before use. ESR spectra were obtained at 77 K (toluene glass) on a Varian E 3 spectrometer with diphenylpicrylhydrazyl as an external standard. ^1H NMR spectra (300 MHz) were recorded on a Bruker WM 300 spectrometer equipped with a low-temperature unit.[9] Chemical shifts are referenced to internal $C_6D_5CD_2H$ (δ = 2.03). No corrections were made.

Preparations and Reactions. (Bicyclo[2.2.1]heptadiene)bis[tris(trimethylphosphine)cobalt] (2). Method a. Anhydrous cobalt chloride (1.07 g, 8.2 mmol), trimethylphosphine (2.4 mL, 24.6 mmol), and norbornadiene (0.42 mL, 4.1 mmol) in 40 mL of tetrahydrofuran were reacted with 1 g of magnesium turnings (excess). Two hours after the start of the reaction, the reddish brown solution was evaporated to dryness. The residue was extracted with three 10-mL portions of pentane. Crystallization at −78 °C gave dark red crystals (2.09 g, 77%) that

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Table I. Atomic Parameters for Compound 2

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
(a) Positional Parameters for Non-Hydrogen Atoms							
Co	0.00335 (6)	0.1078 (1)	0.15095 (3)	C(6)	0.1421 (7)	−0.078 (2)	0.1032 (4)
P(1)	0.0039 (2)	0.2936 (3)	0.10374 (7)	C(7)	−0.1447 (7)	−0.179 (1)	0.1182 (4)
P(2)	0.1282 (2)	−0.0104 (3)	0.15870 (7)	C(8)	−0.1349 (7)	−0.069 (1)	0.0330 (3)
P(3)	−0.1198 (2)	−0.0100 (3)	0.09650 (7)	C(9)	−0.2359 (6)	0.075 (1)	0.0752 (4)
C(1)	0.0126 (9)	0.278 (1)	0.0437 (4)	C(10)	0	0.006 (1)	0.25
C(2)	0.0955 (8)	0.425 (1)	0.1350 (4)	C(11)	0.0789 (5)	0.1171 (9)	0.2700 (2)
C(3)	−0.0938 (8)	0.416 (1)	0.0830 (4)	C(12)	0.0521 (6)	0.2088 (9)	0.2214 (3)
C(4)	0.2444 (6)	0.068 (1)	0.1944 (5)	C(13)	−0.0488 (6)	0.2069 (9)	0.1954 (2)
C(5)	0.1529 (8)	−0.173 (1)	0.1956 (5)				
(b) Hydrogen Positions (Isotropic $B = 8.0 \times 10^4$ pm^2)							
H(11)	0.013	0.373	0.028	H(61)	0.201	−0.127	0.115
H(12)	0.072	0.232	0.048	H(62)	0.092	−0.143	0.083
H(13)	−0.038	0.224	0.017	H(63)	0.140	0.000	0.080
H(21)	0.094	0.501	0.113	H(71)	−0.092	−0.243	0.135
H(22)	0.161	0.380	0.148	H(72)	−0.167	−0.163	0.144
H(23)	0.097	0.464	0.166	H(73)	−0.192	−0.231	0.090
H(31)	−0.136	0.376	0.061	H(81)	−0.212	−0.111	0.013
H(32)	−0.086	0.504	0.068	H(82)	−0.122	0.001	0.014
H(33)	−0.115	0.438	0.109	H(83)	−0.091	−0.151	0.037
H(41)	0.241	0.167	0.185	H(91)	−0.246	0.110	0.103
H(42)	0.265	0.064	0.231	H(92)	−0.287	0.007	0.057
H(43)	0.289	0.024	0.186	H(93)	−0.244	0.153	0.052
H(51)	0.209	−0.222	0.198	H(100)	−0.001	−0.057	0.277
H(52)	0.164	−0.157	0.231	H(110)	0.144	0.081	0.287
H(53)	0.101	−0.243	0.181	H(120)	0.094	0.255	0.210
				H(130)	−0.088	0.258	0.164

decompose above 135 °C (1 bar of Ar).

Method b. (Cyclopentene)tris(trimethylphosphine)cobalt[3] (0.48 g, 1.35 mmol) and norbornadiene (0.08 mL, 0.7 mmol) in 25 mL of pentane were kept at 25 °C for 30 min. Crystallization as above yielded dark red crystals of **1** in 85% yield.

Anal. Calcd for $C_{25}H_{62}Co_2P_6$: C, 45.06; H, 9.38. Found: C, 44.97; H, 9.30. Mass spectrum (above *m/e* 100): *m/e* 666 (M^+), 379 ($L_3CoC_7H_8^+$), 303 ($L_2CoC_7H_8^+$), 287 (L_3Co^+), 211 (L_2Co^+), 135 (LCo^+).

(Bicyclo[2.2.1]heptadiene)bis[tris(perdeuteriotrimethylphosphine)cobalt] (2D). Method b was employed in the synthesis of **2D** on a smaller scale (5 mmol of $P(CD_3)_3$, obtained from CD_3I[8]); yield 50%.

(η^2-Bicyclo[2.2.1]heptadiene)tris(trimethylphosphine)cobalt (1). Method a. Some crystals of **2** (0.52 g, 0.78 mmol) were dissolved in 20 mL of pentane and cooled to −10 °C. Addition of excess norbornadiene (10 mL, 13.7 mmol) gave a green solution, which was immediately cooled to −78 °C. Green crystals of **1** were isolated; yield 0.39 g, 62%.

Anal. Calcd for $C_{16}H_{35}CoP_3$: C, 50.67; H, 9.30; Co, 15.54. Found: C, 50.87; H, 9.27; Co, 14.9.

Method b. In a similar way, (cyclopentene)tris(trimethylphosphine)cobalt[3] (0.40 g, 1.13 mmol) and a slight excess of norbornadiene (0.13 mL, 1.8 mmol) gave a reddish brown solution. Upon cooling, red-brown crystals of **1** were obtained: yield 89%.

Anal. Calcd for $C_{16}H_{35}CoP_3$: C, 50.67; H, 9.30; Co, 15.54. Found: C, 49.75; H, 9.09; Co, 15.30.

(η^2-Bicyclo[2.2.1]heptene)tris(trimethylphosphine)cobalt (3). Method a. Cobalt chloride (0.50 g, 3.85 mmol), trimethylphosphine (1.13 mL, 11.55 mmol), and norbornene (0.60 g, 6.38 mmol) in 30 mL of tetrahydrofuran were reacted with 0.5 g of magnesium turnings (excess). After 3 h, the volatiles were removed in vacuo and the residue was extracted with three 10-mL portions of pentane. Besides the desired complex, the brownish residue contained tetrakis(trimethylphosphine)cobalt[10] (ca. 20%), which proved difficult to remove by recrystallization.

Method b. (Ethene)tris(trimethylphosphine)cobalt[3] (740 mg, 2.35 mmol) and norbornene (350 mg, 3.72 mmol) in 20 mL of pentane were reacted for 24 h at 20 °C. Reducing the volume to 5 mL and slowly cooling to −78 °C gave turquoise crystals (120 mg, 53%), mp 119 °C.

Anal. Calcd for $C_{16}H_{37}CoP_3$: C, 50.4; H, 9.78; Co, 15.46. Found: C, 50.17; H, 9.76; Co, 15.00. ESR: $g_1 = 2.193$, $A_1 = 42$ G; $g_2 = 2.025$, $A_2 = 73$ G; $g_3 = 1.945$, $A_3 = 62$ G.

Magnetic Susceptibility Measurements. Variable-temperature (4–300 K) magnetic susceptibility measurements on powdered samples (8–9 mg) were carried out on a Faraday balance (at the Institut für Anorganische Chemie der RWTH Aachen) with $HgCo(SCN)_4$ as standard. Details of the apparatus are described elsewhere.[11] Susceptibilities were corrected for the diamagnetism of the molecular system (-285×10^{-11} m^3 mol^{-1}/Co atom;[12] SI units) and a small field dependence (field strength 4×10^5 to 11×10^5 A m^{-1}) at low temperature ($T < 80$ K) by extrapolating χ_g for $1/H \rightarrow 0$.

Crystal Measurements. Cell dimensions were obtained on a Syntex $P2_1$ four-circle diffractometer by centering and subsequent refinement of 15 high-angle reflections from different parts of the reciprocal space at room temperature: $a = 15.743$ (4), $b = 9.291$ (3), $c = 28.777$ (9) Å; $\beta = 116.94$ (2)°. From systematic extinct reflections, space group *Cc* or *C2/c* was inferred. With $Z = 4$, the calculated density is 1.18 g/cm^3. A total of 2956 independent reflections were collected between $2° \leq 2\theta \leq 48°$ (Mo Kα radiation, $\lambda = 71.069$ pm; graphite monochromator). The reflections were treated with an empirical absorption correction (μ(Mo) = 11.8 cm^{-1}) and Lorentz and polarization corrections.

Solution and Refinement of the Structure. The structure was successfully solved and refined by using space group *C2/c*, in which the asymmetric unit contains half of a molecule of **2**. The halves of the molecule are related by a twofold axis of symmetry. The position of the cobalt atom was located by a Patterson function. Subsequent difference Fourier maps revealed the positions of all non-hydrogen atoms and some of the hydrogen atoms. The positions of the remaining hydrogen atoms were calculated according to ideal geometry. Refinement, based on 1939 reflections with $F_o \geq 3.92\sigma(F_o)$, using anisotropic thermal parameters for all non-hydrogen atoms converged to $R_1 = 0.063$ and $R_2 = 0.053$ ($1/w = \sigma(F_o)^2 + 0.000025F_o^2$). The hydrogen parameters were not refined. The final atomic parameters are given in Table I.

Results

Syntheses and Properties. Preparation of norbornadiene complexes of cobalt(0) is readily achieved from (olefin)tris(trimethylphosphine)cobalt[3] by a substitution reaction, which, in pentane at 20 °C, is complete within 5 min:

$$2CoC_5H_8(PMe_3)_3 \xrightarrow[-2C_5H_8]{+2C_7H_8} \underset{\mathbf{1}}{2CoC_7H_8(PMe_3)_3} \xrightarrow[-C_7H_8]{} \underset{\mathbf{2}}{C_7H_8[Co(PMe_3)_3]_2}$$

$$C_5H_8 = \text{cyclopentene}$$

However, the green color of **1** is only observed when a freshly prepared solution containing a fivefold excess of norbornadiene is cooled to −78 °C. At 20 °C, the deep red color of **2** visibly

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Table II. Distances (Å) and Angles (deg) in 2[a]

Co-Co*	5.749 (1)	Co-C(13)	2.027 (8)	C(12)-C(13)	1.417 (12)	P(2)-C(5)	1.784 (12)
Co-P(1)	2.199 (3)	Co-H(100)	2.60	P(1)-C(1)	1.799 (11)	P(2)-C(6)	1.817 (11)
Co-P(2)	2.172 (3)	C(10)-C(11)	1.514 (11)	P(1)-C(2)	1.792 (12)	P(3)-C(7)	1.801 (12)
Co-P(3)	2.158 (3)	C(11)-C(12)	1.526 (10)	P(1)-C(3)	1.786 (13)	P(3)-C(8)	1.816 (10)
Co-C(12)	2.041 (7)	C(11)-C(13)*	1.530 (11)	P(2)-C(4)	1.799 (12)	P(3)-C(9)	1.824 (11)

P(1)-Co-P(2)	101.7 (1)	C(11)-C(10)-C(11)*	94.1 (5)	Co-P(1)-C(1)	123.7 (4)
P(1)-Co-P(3)	101.7 (1)	C(10)-C(11)-C(12)	101.1 (6)	Co-P(1)-C(2)	117.0 (4)
P(2)-Co-P(3)	106.9 (1)	C(10)-C(11)-C(13)*	101.2 (6)	Co-P(1)-C(3)	117.6 (4)
P(1)-Co-C(12)	98.5 (2)	C(11)-C(12)-C(13)	104.0 (7)	Co-P(2)-C(4)	119.5 (4)
P(1)-Co-C(13)	98.6 (2)	C(11)*-C(13)-C(12)	105.5 (6)	Co-P(2)-C(5)	115.6 (4)
P(2)-Co-C(12)	102.4 (2)	C(11)-C(12)-Co	118.5 (5)	Co-P(2)-C(6)	123.2 (4)
P(2)-Co-C(13)	140.5 (2)	C(11)*-C(13)-Co	119.8 (5)	Co-P(3)-C(7)	117.2 (4)
P(3)-Co-C(12)	139.8 (2)	P(1)-Co-H(100)	164.4	Co-P(3)-C(8)	123.2 (4)
P(3)-Co-C(13)	101.6 (2)	P(2)-Co-H(100)	87.8	Co-P(3)-C(9)	117.3 (4)
		P(3)-Co-H(100)	87.0		

[a] An asterisk represents the symmetry operation $-x, y, 0.5 - z$.

dominates. When only equimolar amounts of norbornadiene are used at −78 °C, **2** crystallizes rather than **1**. With perdeuteriotrimethylphosphine ligands, complex **2D** was obtained in a similar synthesis.

2 forms large dark red crystals that are readily soluble in ether or toluene. Solid **2** is air sensitive, while in solution it is oxidized to produce trimethylphosphine oxide and a black solid containing cobalt metal. Under 1 bar of Ar, crystals are stable up to 135 °C.

Complex **2** was found to catalyze the dimerization of norbornadiene[13] at 20 °C, yielding predominantly the trans-exo/exo isomer and thereby removing all excess norbornadiene necessary for the formation of complex **1**.

Consequently, **1** is prepared by cooling a freshly prepared concentrated solution of **2** still containing a 5:1 excess of norbornadiene. At −78 °C green crystals of **1** are formed, which upon warming to 20 °C slowly turn red, giving **2** and norbornadiene dimers even in the solid state. Satisfactory elemental analyses for **1** could only be obtained from fresh samples. By contrast, the related norbornene complex[14] **3** proved easy to synthesize by a similar route:

$$CoC_3H_6(PMe_3)_3 \xrightarrow[-C_3H_6]{+C_7H_{10}} \underset{\mathbf{3}}{CoC_7H_{10}(PMe_3)_3}$$

3 forms green crystals that are thermally stable below 120 °C.

There is an easy access to compounds **2** and **3** using a high-yield one-pot synthesis:

$$CoCl_2 + 3PMe_3 + L' \xrightarrow[-MgCl_2]{+Mg(THF)} \mathbf{2} \text{ or } \mathbf{3}$$

$$L' = C_7H_8 \text{ or } C_7H_{10}$$

(Diolefin)bis(trimethylphosphine)cobalt(0) complexes[3] fail to react with norbornadiene to give an η^4-bonded compound that could be favored by the absence of a third phosphine ligand.

$$CoL''(PMe_3)_2 + C_7H_8 \rightarrow Co(C_7H_8)(PMe_3)_2 + L''$$

$$L'' = 1,5\text{-cyclooctadiene, } [Me_2(CH_2{=}CH)Si]_2O$$

$$\mathbf{2} + 2[Me_2(CH_2{=}CH)Si]_2O \rightarrow 2Co[Me_2(CH_2{=}CH)Si]_2O(PMe_3)_2 + 2PMe_3$$

If tetramethyldivinyldisiloxane is used as a diolefin ligand possessing an adjustable bite angle (via deformation of the angle SiOSi),[3] ligand exchange tends to the opposite direction, giving (diolefin)bis(trimethylphosphine)cobalt and liberating the third phosphine.

ESR spectra are obtained from all three compounds in toluene glass (77 K). While compounds **1** and **3** have characteristic 24-line spectra ($I_{Co} = {}^7/_2$) of their own, **2** displays a low-intensity signal that is identical with that of **1**. Apparently, **1** is a product of some oxidative decomposition. **2** itself either does not show an ESR signal or is not detected due to line broadening (Figure 1).

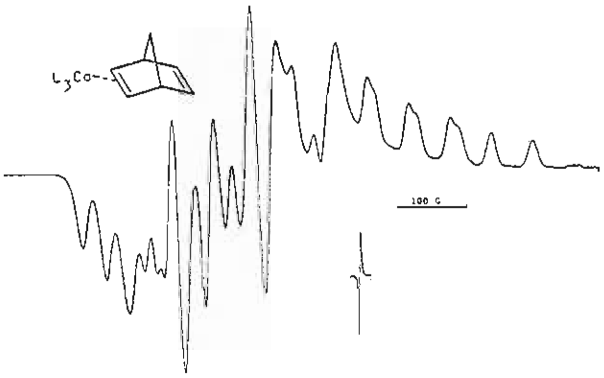

Figure 1. ESR spectrum of **1** (3150 G, 77 K, toluene glass): $g_1 = 2.20$, $A_1 = 37$ G; $g_2 = 2.06$, $A_2 = 42$ G; $g_3 = 1.98$, $A_3 = 65$ G.

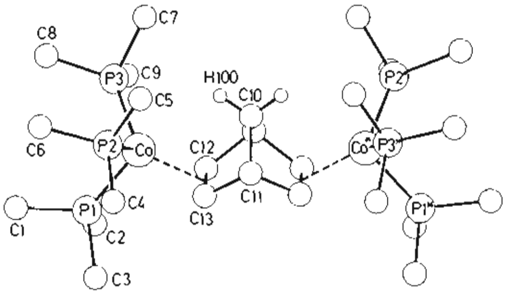

Figure 2. Perspective drawing of **2**.

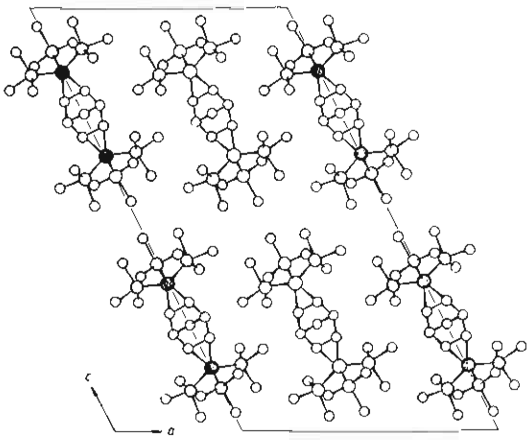

Figure 3. *b*-Axis projection showing the packing of **2** (The dotted Co atoms are located at $y/b = \pm 0.1078$; the other Co atoms, at $y/b = {}^1/_2$ ● 0.1078).

Solid-State Structure of 2. The results of an X-ray structure determination of **2** are given in Tables I and II. As shown in

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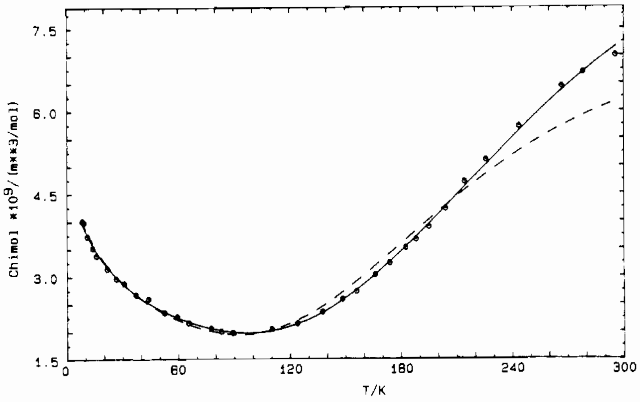

Figure 4. χ_{mol}–T diagram for **2**: ···, experimental values; - - -, best fit with model 3; —, best fit including intermolecular exchange interactions (SI units).

Figure 2, the two $(Me_3P)_3Co$ moieties are coordinated to the double bonds of norbornadiene (NBD) in an exo/exo manner. The halves of the complex are related by a crystallographic twofold axis of symmetry that passes through the bridgehead atom C(10). Figure 3 shows a projection of the unit cell along the b axis. π coordination of the olefinic double bonds to the cobalt atoms gives rise to geometrical adjustments that are typical for transition-metal–olefin complexes:[15] in uncoordinated NBD the C=C distances are 1.343 (3) Å,[16] while they are lengthened to 1.417 (12) Å in **2**. Comparable bond lengths for η^2-coordinated NBD are found in $(\eta^5\text{-}C_5H_5)(CO)_2Mn(\eta^2\text{-NBD})$ (1.404 (4) Å)[17] and $[(dien)Cu(\eta^2\text{-NBD})]BPh_4$ (dien = triethylenediamine) (1.38 (2) Å).

There are two additional differences in the structural parameters. In **2** the dihedral angle between the planes C(11),C(12),C(13),C(11)* and C(11),C(13)*, C(12)*,C(11)* (109.0°) and the distance C(10)–C(11) (1.514 (11) Å) are somewhat smaller than in uncoordinated NBD. However, these parameters from electron diffraction studies of NBD are associated with rather high limits of error and vary considerably, if several independent studies are compared (dihedral angle 110.8–115.6°; C–C distance 1.514–1.575 Å).[16] Whether these structural parameters are indeed affected by π coordination to the metal therefore is questionable.

When an olefin is coordinated to a metal, the substituents at the C=C double bond bend away from the metal.[15] In **2** therefore, the C(11),C(12),C(13),C(11)* plane is not perpendicular to the plane Co,C(12),C(13). However, the observed dihedral angle of 115.3° seems to be quite large,[15] indicating that steric interaction between the methylene bridge of NBD (C(10)) and the $(Me_3P)_3Co$ moiety plays an additional role. This interaction also results in a rather close Co–H(100) approach (2.60 Å), which, to a varying extent, is also observed in $(\eta^5\text{-}C_5H_5)(CO)_2Mn(\eta^2\text{-NBD})$ (Mn–H = 2.97 Å)[17] and $[(dien)Cu(\eta^2\text{-NBD})]BPh_4$ (Cu–H = 2.01 Å).[18] The structure of the latter compound is closely related to that of **2**. In both complexes there are major deviations from a tetrahedral coordination geometry at the metal due to metal–hydrogen interaction. The $(Me_3P)_3Co$ fragment in **2** is tilted in such a way as to place one of the phosphine ligands in an approximately trans position to H(100) (P(1)–Co–H(100) = 164.4°). As a result, there are different P–Co–olefin angles for P(1) vs. P(2) and P(3), respectively (see Table II). A very similar distortion at cobalt is observed in $Li[(Me_3P)_3Co(C_2H_4)]$,[19] because of Co–Li interactions. In this complex both the Co–P and Co–C distances are a few picometers shorter than in **2**, due to the lower oxidation state of the metal.

Magnetic Properties. The χ_{mol}–T diagram of Figure 4 shows the result of the measurements. The observed behavior is typical for a binuclear complex with antiferromagnetically coupled electrons. Starting at room temperature, the susceptibility values decrease with decreasing temperature. (The increase at $T < 80$ K is due to small paramagnetic impurities of a monomer.) Because of the strong coupling of the two electrons, a maximum in the χ_{mol}–T curve is not observed up to room temperature.

We have tried to interpret the data in terms of the isotropic or Heisenberg Hamiltonian

$$H_{ex} = -2JS_a \cdot S_b \qquad (1)$$

for $S_a = S_b = {}^1/_2$ and the so-called Bleaney–Bowers formula[20]

$$\chi'_{mol} = (Ng^2\mu_B{}^2/3kT)[1 + {}^1/_3 \exp(-2J/kT)]^{-1} \qquad (2)$$

where N, g, μ_B, and k are the Avogadro's number, g factor, Bohr magneton, and Boltzmann constant, respectively. $2J$ is the separation between the singlet and the triplet state.[21] In order to take into consideration small amounts (α) of the monomer **1** (assuming Curie or Curie–Weiss behavior) and the temperature-independent paramagnetism (χ_0), two terms were added to the formula:

$$\chi_{mol} = (1 - \alpha)(\chi'_{mol} + \chi_0) + \alpha C/(T - \Theta) \qquad (3)$$

During all the fitting procedures, the g value from the ESR experiment on **1** ($\bar{g}_{av} = 2.075$) and C ($= 0.4712 \times 10^{-5}$ m^3 K mol^{-1}) were held constant. The best fit to the data with model 3 (see broken line in Figure 4) yielded the parameter values $J = -241$ cm^{-1}, $\chi_0 = 80 \times 10^{-11}$ m^3 mol^{-1}, $\alpha = 0.0280$, and $\Theta = -32.8$ K. Figure 4 illustrates that the fit is poor in the high-temperature region. The calculated susceptibilities are smaller than the experimental results. In general, deviation from model 3 is found if (i) a combined effect of crystal field and spin–orbit coupling is present, (ii) exchange interactions exist between the binuclear units, (iii) the susceptibility of the monomer impurity shows a remarkable temperature dependence, and (iv) J is temperature dependent. To start with condition i, effects of anisotropy can be included by using the approach of Nakatsuka et al.[22] for the XY–Heisenberg and the Ising–Heisenberg case. Calculations based on these models, however, did not significantly improve the fit with physically reasonable parameters.

Taking into consideration intermolecular exchange interactions (condition ii) in the molecular field approximation (with the molecular field parameter λ[23]), a good fit can be achieved with the parameter values $J = -261$ cm^{-1} and $\lambda = 419 \times 10^5$ mol m^{-3} and nearly unchanged values for χ_0, α, and Θ (see solid line in Figure 4). But the relatively large positive value for λ indicates strong ferromagnetic exchange interactions between the binuclear units. This seems unreasonable because of the large intermolecular Co–Co distances (860–930 pm) and the lack of a suitable pathway for the interactions (see Figure 3). As for the behavior of the monomer impurity (condition iii), it is known from susceptibility data for 3d^9 mononuclear complexes that it cannot be responsible for the observed deviation from the extended Bleaney–Bowers formula. Lastly, assuming a temperature-dependent singlet–triplet splitting (condition iv), it follows from experiment that $|J|$ must decrease with increasing temperature. The variation of J with temperature could be determined by using at first only experimental data for $T < 180$ K. In this temperature region a good fit with model 3 can be achieved with the parameter values $J = -249$ cm^{-1} and $\chi_0 = 87 \times 10^{-11}$ m^3 mol^{-1} and with α and Θ the same as before. In the region $T > 180$ K, J was determined separately for each experimental value with all other parameters constant. The results of these calculations are seen in Figure 5, which shows the decrease of $|J|$ from 249 cm^{-1} at $T < 180$ K to 220 cm^{-1} at room temperature.

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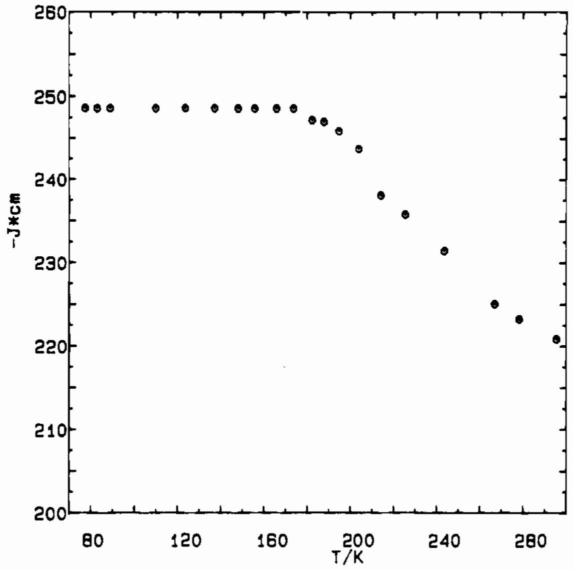

Figure 5. Temperature dependence of J.

Table III. ^{1}H NMR Shifts of 2

T/K	δ[≡CH][a]	δ[P(CH$_3$)$_3$]	δ[>CH]	δ[imp]
296	−2.05	8.85	15.15	74.30
283	−1.65	8.37	14.70	79.10
263	−1.44	8.07	14.56	81.85
243	−1.09	7.43	13.96	87.10
223	−0.40	6.25	13.00	97.52
203	+0.20	5.22	12.30	106.54

[a] Chemical shifts are referenced to internal $C_6D_5CD_2H$ (δ = 2.03).

Table IV. Comparison of Magnetic Susceptibility Data and ^{1}H NMR Shifts of 2

magnetic susceptibility[a]		^{1}H NMR shifts[b]			
T/K	$10^9\chi_{mol}$/ m^3 mol^{-1}	T/K	δ[≡CH]	δ-[P(CH$_3$)$_3$]	δ[>CH]
295.5	6.50	296	6.50	6.50	6.50
278.3	6.16	283	7.77	6.14	6.30
266.9	5.88	263	8.43	5.93	6.25
243.7	5.09	243	9.54	5.45	5.98
225.6	4.44	223	11.70	4.59	5.58
214.2	3.98	203	13.60	3.83	5.28
204.0	3.46				
195.0	3.08				

[a] Magnetic susceptibility/Co atom (SI units), without monomer contribution. [b] Chemical shifts (see Table III) based on the room-temperature value of $10^9\chi_{mol}$ for 2.

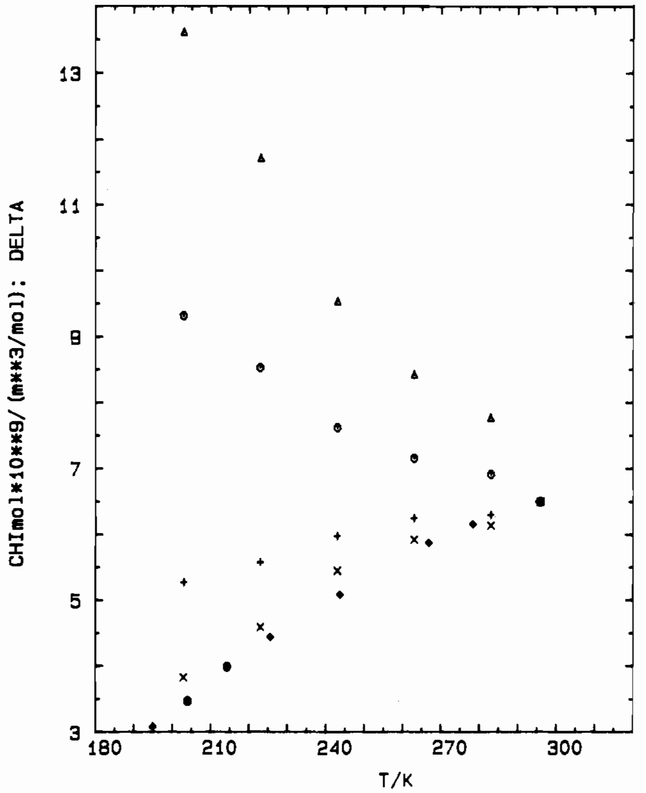

Figure 6. Magnetic susceptibilities of **2** without monomer contribution and paramagnetic shifts (from Table III) based on the room-temperature value of $10^9\chi_{mol}$: ◊, χ_{mol}; ×, δ[PCH$_3$]; +, δ[≥CH]; △, δ[≡CH]; ○, impurity.

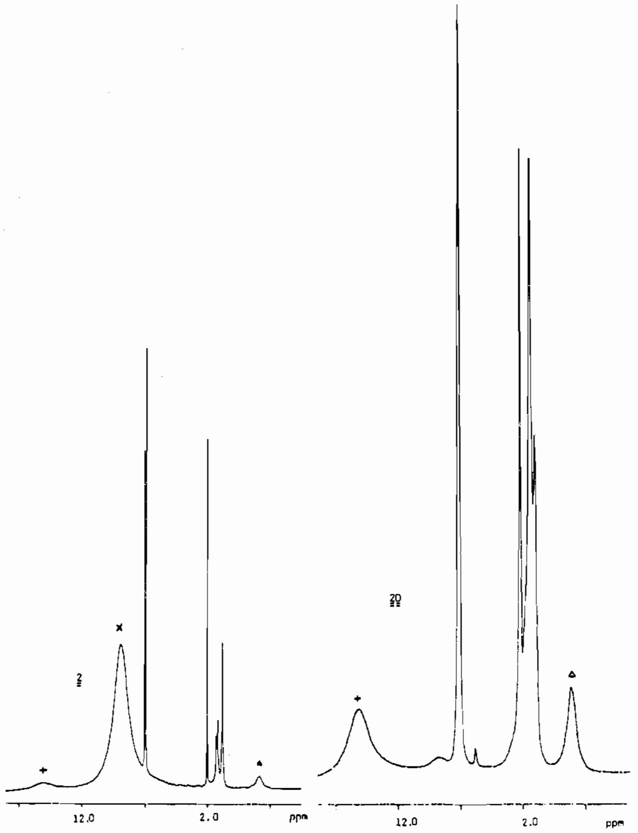

Figure 7. ^{1}H NMR spectra of **2** and **2D** (300 MHz; 2% and 10% in toluene-d_8, respectively; 296 K). Assignments are as in Figure 6.

A comparison of solid-state magnetic properties with the solution behavior of compound **2** was attempted by using paramagnetic proton resonance at variable temperature. Table III gives the temperature NMR shifts of the ligand protons. In Table IV and Figure 6 are shown the magnetic susceptibility data of **2** (without monomer contribution) and the NMR shifts based on the room-temperature value of χ_{mol}.

The assignment of two observable C_7H_8 proton resonances in **2** out of three (2 H, 2 H, 4 H) is based on the spectrum of the free ligand and a close correspondence of signals with those of **2D** (Figure 7). At room temperature their positions are at δ 15.15, −2.05 and δ 15.5, −1.95 for **2** and **2D**, respectively. A third resonance at δ 74.3 showing Curie behavior with temperature should arise from the PCH$_3$ resonance of a mononuclear complex (which is probably **1**) because no resonance at this position is obtained from **2D**.

After a careful but unsuccessful search (Me$_4$Si region ± 200 ppm) we conclude that the missing resonance (2 H) is most likely that of H(100) (Figure 2), which between −80 and +25 °C is broadened below the threshold of detection. A close approach of H(100) to a cobalt nucleus (I = $^7/_2$) might offer an explanation, although spin–spin contacts even through Co–H σ-bonds as in

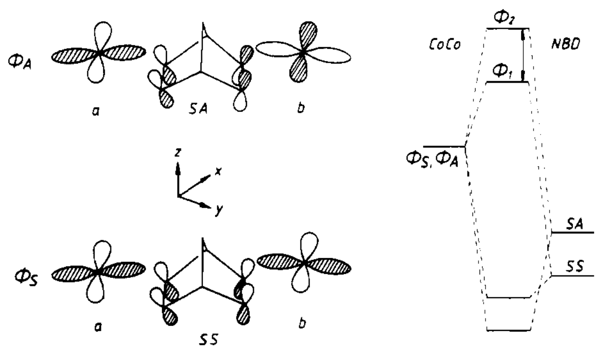

Figure 8. Orbital model in analogy to that of Hoffmann et al.[26] applied to the [Co–norbornadiene–Co] unit. S and A refer to mirror planes[5].

diamagnetic $CoHL'L_3$ ($L = PMe_3$; $L' = L$, olefin) do not usually cause extreme line broadening.

However, from the observed resonances it is obvious that the NMR shifts differ widely in magnitude as well as in temperature dependence. The shifts of the phosphine protons with temperature, for instance, are very similar to the magnetic behavior of the binuclear unit in the crystal (see Figure 6).

Discussion

The two results of our magnetochemical investigation are the large singlet–triplet splitting and the obviously existing temperature dependence of this splitting.

From proton magnetic resonance experiments, the temperature dependence of the contact shifts may be utilized in a qualitative fashion to demonstrate the spin pairing as the temperature is lowered. Departures of the contact shifts of ligand protons (e.g. of the trimethylphosphines) from a strict Curie dependence can be very close to those of the magnetic moments, indicating mainly intramolecular contact interactions[24] in the crystal and in solution.

The observed singlet–triplet separation in spite of the large Co–Co distance must be due to the π-electron systems of the norbornadiene bridging ligand. According to the investigations of Hoffmann[5] one should expect significant overlap between the π orbitals of the norbornadiene molecule. The delocalized combinations SS and SA after interactions (where SS is the ground state and SA the excited state) are shown in Figure 8. These doubly occupied states, which show an energy separation of about 0.85 eV in the free ligand,[25] must be responsible for the superexchange mechanism between the d^9 centers.

Because of the nearly tetrahedral environment of the metal atoms, the unpaired electrons are assumed to be in the d_{xy} orbitals. These are oriented toward the double bonds and can form σ-bonds with SS and SA. In a simple molecular orbital description it is sufficient to consider the two highest occupied levels only, which can be formed from the two linear combinations of the d_{xy} orbitals:

$$\Phi_S \sim d_{xy}(a) + d_{xy}(b) \qquad \Phi_A \sim d_{xy}(a) - d_{xy}(b)$$

(a and b are related to the two metal centers.) In the case of noninteracting metal atoms these states are equal in energy. In the binuclear unit the symmetric combination Φ_S can interact with SS and the antisymmetric combination Φ_A with SA. Since the metal 3d orbitals are closer in energy to SA than to SS, Φ_A is shifted upward (E_2) more than Φ_S (E_1). In analogy to the approach of Hay, Thibeault, and Hoffmann,[26] the singlet–triplet $E_T - E_S$ difference is given by

$$E_T - E_S = -2J = -2K_{ab} + \frac{(E_1 - E_2)^2}{J_{aa} - J_{ab}}$$

where K_{ab}, J_{aa}, and J_{ab} are exchange and Coulomb integrals, respectively. K_{ab} is a small quantity and can in general be ignored besides the other terms. This means the singlet is stabilized if a significant splitting between the molecular orbitals Φ_S and Φ_A after interaction is present. Hence, the observed relatively large singlet–triplet splitting in the Co binuclear complex must be a consequence of the strong interaction between the π-electron systems of the bridging ligand.

From these ideas, it follows that the splitting must be very sensitive to geometrical modifications of the norbornadiene bridge, especially of the dihedral angle between the planes C(11),C(12),C(13),C(11)* and C(11),C(13)*,C(12)*,C(11)* (see Figure 2). Assuming for instance a small increase of this angle with increasing temperature, the singlet–triplet splitting should decrease in accordance with the experimental results.

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Supplementary Material Available: Observed and calculated structure factors (Table A), anisotropic parameters for non-hydrogen atoms (Table A′), and magnetic susceptibility data for **2** (Table B) (17 pages). Ordering information is given on any current masthead page.

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(24) Some contribution to the total paramagnetic shift from dipolar contact interactions cannot be excluded. This will depend on the anisotropy of the **g** tensor. Although a noticeable anisotropy in **2** is inferred from the ESR spectrum of **1** (Figure 1), the effect is assumed to be small.

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