interatomic distances (Table IIA) and bond angles (Table IIIA) in the disordered $[Co(\eta^4\text{-}C_4H_6)(PMe_3)_3]^+$ cations, refined temperature factors (Table VI), calculated coordinates of the hydrogens atoms of the phenyl rings (Table VII), geometry of the BPh_4^- ions (Table VIII), weighted least-squares planes (Table IX), and observed and calculated structure factor amplitudes (Table X) (65 pages). Ordering information is given on any current masthead page.

Triptycene π Complexes. Molecular Structures of $(C_{20}H_{14})Cr(CO)_3$ and $(C_{20}H_{14})Co_4(CO)_9$

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The crystal and molecular structures of tricarbonyl(η^6-triptycene)chromium (1) and nonacarbonyl(η^6-triptycene)tetracobalt (2) have been determined. Crystals of 1 are monoclinic, space group $P2_1/c$ (no. 14), with $a = 13.590$ (1) Å, $b = 13.403$ (3) Å, $c = 10.286$ (1) Å, $\beta = 109.18$ (1)°, and $Z = 4$. Crystals of 2 are monoclinic, space group $C2/c$ (no. 15), with $a = 31.033$ (6) Å, $b = 14.467$ (1) Å, $c = 12.183$ (1) Å, $\beta = 93.03$ (1)°, and $Z = 8$. Deformations in the molecular structures are consistent with the operation of a steric effect involving nonbonded repulsion between one of the triptycene rings and the $Cr(CO)_3$ and $Co_4(CO)_9$ tripods. Because of the greater steric demand of $Co_4(CO)_9$, the observed effect is markedly more pronounced in 2 than in 1.

Transition-metal π complexes of bulky arenes exhibit stereochemical features of exceptional interest; examples are the conformational variability in chromium complexes of hexaethylbenzene[2] and restricted rotation about the arene-metal bond in a ruthenium complex of 1,4-di-*tert*-butylbenzene.[3] Some years ago, Pohl and Willeford[4] suggested the possibility of restricted rotation about the benzene–chromium bond in tricarbonyl(η^6-triptycene)chromium (1) but noted that the barrier to rotation "could be reduced considerably, either by a tilting of the tricarbonylchromium with respect to the plane of the ring to which it is bonded, or by significant distortion of the triptycene molecule itself". The present work was undertaken in order to determine whether such distortions have a significant effect on the ground-state structure of 1.[5] In addition we also determined the structure of nonacarbonyl(η^6-triptycene)tetracobalt (2), a compound in which the deformations described by Pohl and Willeford are expected to be substantially more severe. Prior to the present work, no X-ray structures of triptycene π complexes had been reported.

Experimental Section

Infrared spectra were recorded on a FTS-20C Digilab FT-IR spectrometer. ^1H NMR spectra were recorded on a Bruker WM 250 spectrometer. All reported chemical shifts are reported in parts per million downfield relative to tetramethylsilane. Reagents were obtained from Strem Chemicals (dicobalt octacarbonyl and chromium hexacarbonyl) and Aldrich (triptycene). Hexane, pentane, and benzene were distilled from sodium-benzophenone and purged with argon before reaction. All reactions were carried out in an inert (argon) atmosphere.

Tricarbonyl(η^6-triptycene)chromium (1) was prepared as described previously.[4] The product was purified by column chromatography on neutral alumina, eluting first with hexane, to remove triptycene, and then with benzene. Crystals suitable for X-ray analysis were grown by layering a concentrated solution of 1 in benzene with an equal volume of hexane and allowing the solutions to diffuse slowly in the dark at room temperature: yellow crystals; mp 232–236 °C dec (lit.[4] mp 235–236 °C dec; lit.[6] mp 237 °C dec); IR (cyclohexane) 1975 (s), 1913 (s) cm^{-1} (lit.[4] 1975, 1910 cm^{-1}; lit.[6] 1974, 1906 cm^{-1}). The ^1H NMR spectrum ($CDCl_3$, ambient temperature) featured an apparent singlet, corresponding to the aliphatic bridgehead protons (δ 5.14 (2 H)), and three pairs of multiplets, corresponding to the AA′ and BB′ portions of the aromatic protons in each of the three rings (and identified as such by decoupling experiments): set 1 (δ 5.04–5.10 (2 H) and 5.66–5.73 (2 H)), set 2 (δ 6.97–7.04 (2 H) and 7.31–7.37 (2 H)), and set 3 (δ 7.07–7.15 (2 H) and 7.37–7.42 (2 H). Pohl and Willeford[4] report a bridgehead singlet at δ 5.18 and two "A_2B_2 patterns" centered at δ 5.40 and 7.28. Moser and Rausch[6] report a bridgehead singlet at δ 5.10, a multiplet for the aromatic protons of the complexed ring centered at δ 5.30, and a multiplet for the aromatic protons of the two uncomplexed rings centered at δ 7.15.

Nonacarbonyl(η^6-triptycene)tetracobalt (2). A solution of triptycene (0.51 g, 2 mmol) and tetracobalt dodecacarbonyl (0.57 g, 1 mmol) in a mixture of dodecane (1.5 mL) and dioxane (1.5 mL) was heated for 8 min at 125–130 °C while a slow stream of argon was maintained through the solution. The solution was cooled, diluted with pentane (10 mL), and chromatographed on Florisil. Elution of the unreacted $Co_4(CO)_{12}$ with hexane (violet band) was followed by elution with 1:1 v/v hexane–benzene and benzene to recover the desired product (green band). The eluate was evaporated, and the residue (0.7–2.1 mg, 0.1–0.3% yield) was dissolved in pentane. Crystals suitable for X-ray analysis were obtained by cooling the pentane solution (containing, if necessary, a small amount of benzene to increase the solubility). The greenish black crystals decompose above 180 °C: IR (cyclohexane) 2068 (m), 2049 (w), 2025 (s), 2004 (m), 1990 (s), 1892 (s), 1885 (s), 1841 (s), 1826 (s). The ^1H NMR spectrum ($CDCl_3$, ambient temperature) featured an apparent singlet, corresponding to the aliphatic

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(2) (a) Hunter, G.; Iverson, D. J.; Mislow, K.; Blount, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5942. (b) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *Ibid.* **1981**, *103*, 6073. (c) Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Iverson, D. J.; Mislow, K. *Organometallics* **1982**, *1*, 448. (d) Hunter, G.; Wadsworth, W. S., Jr.; Mislow, K. *Ibid.* **1982**, *1*, 968. (e) Blount, J. F.; Hunter, G.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1984**, 170.

(3) Pomeroy, R. K.; Harrison, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 661.

(4) Pohl, R. L.; Willeford, B. R. *J. Organomet. Chem.* **1970**, *23*, C45.

(5) Professor Willeford kindly encouraged us to proceed with this work since his own intended X-ray study of 1[4] had failed to materialize (Willeford, B. R., private communication).

(6) Moser, G. A.; Rausch, M. D. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 37.

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bridgehead protons (δ 5.43 (2 H)), and three pairs of well-separated multiplets, corresponding to the AA′ and BB′ portions of the aromatic protons in each of the three rings (and identified as such by decoupling experiments): set 1 (δ 6.04–6.13 (2 H) and 6.41–6.49 (2 H)), set 2 (δ 6.74–6.82 (2 H) and 7.07–7.16 (2 H)), and set 3 (7.28–7.38 (2 H) and 7.71–7.80 (2 H)).

Crystallography. The intensity data for 1 and 2 were measured on a Enraf-Nonius CAD4 diffractometer [graphite-monochromated Cu Kα radiation (λ = 1.541 84 Å), ω–2θ scans], and the data were corrected for absorption by an analytical procedure.[7] The structures were solved by a combination of direct methods and traditional Fourier techniques. The scattering curves for Cr^0 and Co^0 were both corrected for the real and imaginary parts of the anomalous dispersion. Full-matrix least squares was used for all refinements. In the final refinements, the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in the structure factor calculations but were not refined. The positions of the hydrogen atoms were calculated, based on the usual trigonal and tetrahedral geometry of the carbon atoms. The refinements were stopped when all shifts were less than one-fourth of the corresponding estimated standard deviations.

Crystals of 1 are monoclinic, space group $P2_1/c$, with a = 13.590 (1) Å, b = 13.403 (3) Å, c = 10.286 (1) Å, β = 109.18 (1)°, μ = 57.6 cm^{-1}, and d_{calcd} = 1.465 g cm^{-3} for Z = 4 ($Cr(CO)_3C_{20}H_{14}$, M = 390.36). The size of the crystal used for data collection was approximately 0.15 × 0.15 × 0.30 mm (0.57 > τ > 0.38). A total of 2616 independent reflections were measured for $\theta < 60°$, of which 2055 were considered to be observed [$I > 3\sigma(I)$]. The final discrepancy indices are R = 0.039 and wR = 0.046 for the 2055 observed reflections (8.4 observations/parameter). The final difference map has no peaks greater than ±0.7 e Å^{-3}.

Crystals of 2 are monoclinic, space group $C2/c$, with a = 31.033 (6) Å, b = 14.467 (1) Å, c = 12.183 (1) Å, β = 93.03 (1)°, μ = 187.4 cm^{-1}, and d_{calcd} = 1.805 g cm^{-3} for Z = 8 ($Co_4(CO)_9C_{20}H_{14}$, M = 742.16). The size of the crystal used for data collection was approximately 0.06 × 0.06 × 0.09 mm (0.40 > τ > 0.29). A total of 2806 independent reflections were measured for $\theta < 50°$, of which 1302 were considered to be observed [$I > 3\sigma(I)$]. The final discrepancy indices are R = 0.028 and wR = 0.027 for the 1302 observed reflections (3.4 observations/parameter). The final difference map has no peaks greater than ±1.0 e Å^{-3}.

Results and Discussion

The tricarbonylchromium and nonacarbonyltetracobalt complexes of triptycene were prepared by reaction of triptycene with chromium hexacarbonyl and tetracobalt dodecacarbonyl, respectively. Because complexation reduces the symmetry of triptycene from D_{3h}[8] to at most C_s, three AA′BB′ multiplets are observed in the aromatic region of the ^1H NMR spectrum (solvent $CDCl_3$). In tricarbonyl(η^6-triptycene)chromium (1), the two downfield multiplets centered at δ 7.17 and 7.25 correspond to the protons in the two uncomplexed rings[9] and the multiplet at δ 5.38 to the protons in the complexed ring; the upfield shift is of the expected order of magnitude.[10,11] In nonacarbonyl(η^6-triptycene)tetracobalt (2), the three aromatic multiplets are now centered at δ 6.27, 6.95, and 7.54. While the upfield shift of the protons in the complexed ring is

Table I. Final Atomic Parameters for 1[a]

atom	x	y	z	B_{eqv}, Å^2
Cr	0.43576 (4)	0.38698 (5)	0.67815 (6)	2.64 (2)
O(1)	0.3216 (2)	0.1931 (2)	0.6208 (3)	4.5 (1)
O(2)	0.3319 (2)	0.4377 (3)	0.3814 (3)	5.8 (2)
O(3)	0.6119 (3)	0.3083 (3)	0.5951 (4)	7.4 (2)
C(1)	0.3676 (3)	0.2674 (3)	0.6417 (4)	3.1 (2)
C(2)	0.3719 (3)	0.4200 (3)	0.4962 (4)	3.6 (2)
C(3)	0.5441 (3)	0.3381 (3)	0.6284 (5)	4.2 (2)
C(11)	0.3561 (3)	0.5119 (3)	0.7492 (3)	2.4 (1)
C(12)	0.4547 (3)	0.5445 (3)	0.7504 (4)	2.9 (1)
C(13)	0.5434 (3)	0.4905 (3)	0.8237 (4)	3.1 (2)
C(14)	0.5343 (3)	0.4025 (3)	0.8952 (4)	3.1 (2)
C(15)	0.4354 (3)	0.3689 (3)	0.8905 (3)	2.8 (2)
C(16)	0.3463 (3)	0.4249 (3)	0.8183 (3)	2.4 (1)
C(21)	0.1790 (3)	0.4893 (3)	0.5900 (3)	2.9 (2)
C(22)	0.1268 (3)	0.5001 (3)	0.4513 (4)	3.6 (2)
C(23)	0.0657 (3)	0.4223 (4)	0.3795 (4)	4.5 (2)
C(24)	0.0575 (3)	0.3351 (3)	0.4462 (5)	4.3 (2)
C(25)	0.1091 (3)	0.3246 (3)	0.5865 (4)	3.7 (2)
C(26)	0.1695 (3)	0.4021 (3)	0.6572 (4)	2.8 (1)
C(31)	0.2110 (3)	0.5824 (3)	0.8038 (4)	3.0 (2)
C(32)	0.1843 (3)	0.6732 (3)	0.8452 (4)	3.9 (2)
C(33)	0.1453 (3)	0.6752 (4)	0.9555 (5)	5.0 (2)
C(34)	0.1351 (3)	0.5890 (4)	1.0211 (5)	5.0 (2)
C(35)	0.1631 (3)	0.4975 (3)	0.9799 (4)	4.1 (2)
C(36)	0.2006 (3)	0.4950 (3)	0.8704 (4)	3.1 (2)
C(40)	0.2519 (3)	0.5645 (3)	0.6833 (4)	2.9 (1)
C(47)	0.2337 (3)	0.4023 (3)	0.8094 (4)	2.7 (1)

[a] Standard deviations in parentheses. Parameters for hydrogen atoms and anisotropic thermal parameters are given in the supplementary material.

Table II. Bond Lengths in 1[a]

Cr–C(1)	1.828 (4)	C(21)–C(22)	1.376 (5)
Cr–C(2)	1.839 (4)	C(21)–C(26)	1.385 (5)
Cr–C(3)	1.831 (5)	C(21)–C(40)	1.514 (5)
		C(22)–C(23)	1.385 (6)
O(1)–C(1)	1.158 (5)	C(23)–C(24)	1.379 (7)
O(2)–C(2)	1.151 (5)	C(24)–C(25)	1.389 (6)
O(3)–C(3)	1.155 (6)	C(25)–C(26)	1.375 (5)
		C(26)–C(47)	1.521 (5)
C(11)–C(12)	1.405 (5)	C(31)–C(32)	1.377 (6)
C(11)–C(16)	1.395 (5)	C(31)–C(36)	1.388 (6)
C(11)–C(40)	1.527 (5)	C(31)–C(40)	1.535 (6)
C(12)–C(13)	1.396 (5)	C(32)–C(33)	1.401 (7)
C(13)–C(14)	1.417 (6)	C(33)–C(34)	1.369 (8)
C(14)–C(15)	1.403 (5)	C(34)–C(35)	1.390 (7)
C(15)–C(16)	1.410 (5)	C(35)–C(36)	1.381 (6)
C(16)–C(47)	1.533 (5)	C(36)–C(47)	1.525 (6)

[a] In angstrom units. Standard deviations in parentheses.

Table III. Bond Angles in 1[a]

C(1)–Cr–C(2)	87.9 (2)	C(23)–C(24)–C(25)	120.5 (4)
C(1)–Cr–C(3)	91.7 (2)	C(24)–C(25)–C(26)	118.9 (4)
C(2)–Cr–C(3)	87.4 (2)	C(21)–C(26)–C(25)	120.7 (3)
Cr–C(1)–O(1)	177.3 (4)	C(21)–C(26)–C(47)	113.3 (3)
Cr–C(2)–O(2)	178.0 (4)	C(25)–C(26)–C(47)	125.9 (3)
Cr–C(3)–O(3)	178.9 (4)	C(32)–C(31)–C(36)	120.9 (4)
C(12)–C(11)–C(16)	120.3 (3)	C(32)–C(31)–C(40)	126.2 (4)
C(12)–C(11)–C(40)	127.1 (3)	C(36)–C(31)–C(40)	112.9 (3)
C(16)–C(11)–C(40)	112.5 (3)	C(31)–C(32)–C(33)	118.4 (4)
C(11)–C(12)–C(13)	119.7 (3)	C(32)–C(33)–C(34)	120.6 (5)
C(12)–C(13)–C(14)	120.3 (3)	C(33)–C(34)–C(35)	120.8 (5)
C(13)–C(14)–C(15)	119.7 (3)	C(34)–C(35)–C(36)	118.8 (4)
C(14)–C(15)–C(16)	119.7 (3)	C(31)–C(36)–C(35)	120.4 (4)
C(11)–C(16)–C(15)	120.2 (3)	C(31)–C(36)–C(47)	113.2 (4)
C(11)–C(16)–C(47)	113.3 (3)	C(35)–C(36)–C(47)	126.4 (4)
C(15)–C(16)–C(47)	126.5 (3)	C(11)–C(40)–C(21)	107.0 (3)
C(22)–C(21)–C(26)	120.4 (3)	C(11)–C(40)–C(31)	104.0 (3)
C(22)–C(21)–C(40)	126.4 (4)	C(21)–C(40)–C(31)	106.4 (3)
C(26)–C(21)–C(40)	113.2 (3)	C(16)–C(47)–C(26)	106.6 (3)
C(21)–C(22)–C(23)	119.2 (4)	C(16)–C(47)–C(36)	103.8 (3)
C(22)–C(23)–C(24)	120.4 (4)	C(26)–C(47)–C(36)	106.1 (3)

[a] In degrees. Standard deviations in parentheses.

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(7) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035.

(8) Anzenhofer, K.; de Boer, J. J. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1970**, *131*, 103. See also: Hazell, R. G.; Pawley, G. S.; Petersen, C. E. L. *J. Cryst. Mol. Struct.* **1971**, *1*, 319.

(9) In triptycene, the aromatic multiplet is centered at δ 7.16 and the bridgehead proton singlet at δ 5.39 ($CDCl_3$). See also: Smith, W. B.; Shoulders, B. A. *J. Phys. Chem.* **1965**, *69*, 2022. Kidd, K. G.; Kotowycz, G.; Schaefer, T. *Can. J. Chem.* **1967**, *45*, 2155. Cooper, M. A.; Manatt, S. L. *J. Am. Chem. Soc.* **1970**, *92*, 1605.

(10) Sneeden, R. P. A. "Organochromium Compounds"; Academic Press: New York, 1975; p 112 ff and references therein.

(11) Emanuel, R. V.; Randall, E. W. *J. Chem. Soc. A* **1969**, 3002. For example, the chemical shifts of the aromatic protons in 1,2-dimethylbenzene and its tricarbonylchromium complex are 7.10 and 5.21–5.27 ppm, respectively.

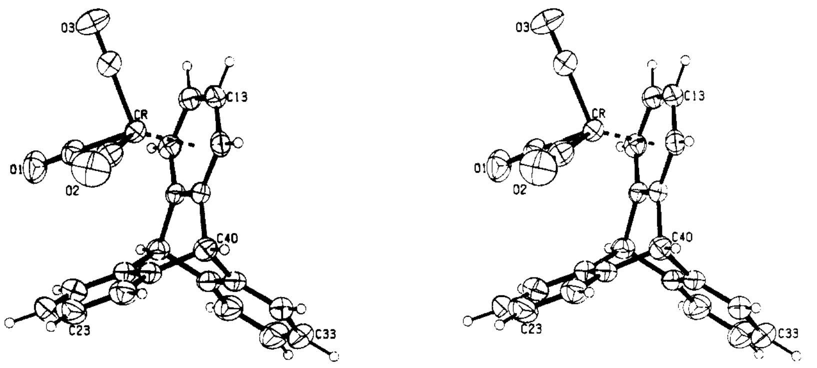

Figure 1. Stereoview of the X-ray structure of tricarbonyl(η^6-triptycene)chromium (1).

similar in magnitude to that found for other complexes of this type,[12] the dispersion of the two sets of downfield signals (0.6 ppm) is a clear indication that one of the two uncomplexed rings in 2 is strongly perturbed by the $Co_4(CO)_9$ group. This conclusion is supported by a comparison of the X-ray structures of 1 and 2.

The crystals of 1 belong to the monoclinic system. The space group is $P2_1/c$, and the four molecules in the unit cell occupy general positions. A stereoview of 1 is shown in Figure 1, final atomic parameters are listed in Table I, and bond lengths and angles are given in Tables II and III. The molecule adopts approximate C_s symmetry. The perpendicular distances of Cr, C(3), and O(3) from the quasi-mirror plane defined by the midpoints of the C(13)–C(14), C(23)–C(24), and C(33)–C(34) lines are −0.044, +0.054, and +0.140 Å, respectively, a positive sign indicating a deviation toward the side containing C(13), C(23), and C(33). Thus, the chromium atom and one of the carbonyl groups lie roughly in the plane. Similarly, the perpendicular distances of C(1), O(1), C(2), and O(2) (−1.436, −2.322, +1.098 and +1.784 Å, respectively) indicate that the other two carbonyl groups straddle the quasi-mirror plane.

In most respects, the molecular structure of 1 exhibits the normal features of an arene tricarbonylchromium complex.[10,13] Like many other such complexes containing two ortho substituents, the carbon atoms in the complexed ring (ring 1 = C(11) to C(16)) are staggered with respect to the carbonyl ligands, with the Cr–C–O vectors pointing roughly toward the midpoints of the C(11)–C(12), C(13)–C(14), and C(15)–C(16) lines. As expected by analogy with other (arene)tricarbonylchromium complexes,[13] the average C–C distance in ring 1 (1.404 Å) is slightly longer than the corresponding distances in ring 2 (1.381 Å), ring 3 (1.384 Å), and triptycene itself[8] (1.389 Å); there is no evidence for bond-length alternation. The average $Cr–C_{CO}$, $Cr–C_{ar}$, and C–O bond distances of 1.833, 2.218, and 1.154 Å, the average $C_{CO}–Cr–C_{CO}$ and Cr–C–O bond angles of 89.0° and 178.0°, and the distance between the Cr atom and the centroid of ring 1, 1.716 Å, also fall within the normal range.[10,13] Nevertheless, a number of deviations from normalcy are observed which, though slight in themselves, in combination tend to suggest the effect of nonbonded interactions between the $Cr(CO)_3$ fragment and ring 2.

Thus, although the $Cr–C_{ar}$ distances average to a normal 2.218 Å, the distances between the Cr atom and the two Cr_{ar}'s in ring 1 that are closest to ring 2 (2.243 and 2.228 Å for Cr–C(11) and Cr–C(16), respectively) are slightly longer than those between Cr and the other C_{ar}'s in ring 1 (2.225, 2.206, 2.204, and 2.199 Å for Cr–C(12), Cr–C(13), Cr–C(14), and Cr–C(15), respectively). Unlike similar $Cr(CO)_3$ slippages in complexes of arenes that are part of condensed systems or that are attached to other aromatic rings,[10,13] the present observations cannot be attributed to π-conjugation effects.[14]

Small deformations in ring 1 may also be significant. Thus, although all three rings are closely approximated by regular hexagons, with average deviations from the least-squares planes of 0.007, 0.004, and 0.004 Å for rings 1, 2, and 3, respectively, each is slightly folded in a boatlike fashion about its midline. In rings 2 and 3 the angle of fold is negligible (ca. 0.5°), but in ring 1 the dihedral angle between the C(12)–C(11)–C(16)–C(15) and C(12)–C(13)–C(14)–C(15) planes is significantly larger (1.5°). Similarly, the dihedral angle between the least-squares plane of ring 1 and the C(40)–C(11)–C(16)–C(47) plane is 3.0°. Both displacements are in a direction away from ring 2, thus providing more room between rings 1 and 2.

A final clue may be found in small but significant deformations of the C–C–C angles subtended at the bridgehead atoms C(40) and C(41). These consist of a closure of the C(11)–C(40)–C(31) and C(16)–C(47)–C(36) angles from 105.3° in triptycene[8] to an average angle of 103.9° and a concomitant opening of the other four C–C–C angles to an average of 106.5°. The effect of these deformations is also to increase the separation of the $Cr(CO)_3$ fragment and ring 2.

All of these observations are consistent with the operation of a steric effect involving nonbonded repulsion between the $Cr(CO)_3$ fragment and ring 2.[15] However, to judge by the magnitude of the deformations, the effect of these repulsive interactions on the ground-state structure of 1 is rather minor.

We now turn to an examination of the structure of 2. The crystals of this complex belong to the monoclinic system. The space group is $C2/c$, and the eight molecules in the unit cell occupy general positions. A stereoview of 2 is shown in Figure 2, and final atomic parameters are listed in Table IV. Like 1, 2 adopts approximate C_s symmetry (Figure 3). The perpendicular distances of the apical cobalt atom Co(1) and of one of the basal atoms,

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[12] Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 1* **1973**, 975.

[13] Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499 and references therein.

[14] It has been suggested that hyperconjugation may contribute to the $Cr(CO)_3$ slippage observed in the π complex of 9,10-dihydrophenanthrene (Muir, K. W.; Ferguson, G. *J. Chem. Soc. B* **1968**, 476). However, no slippage is observed in the *exo*-tricarbonylchromium complex of *exo*-2-acetoxybenzonorbornene, where π-conjugation effects cannot be invoked and where steric effects are not likely to play a significant role (Taylor, I. F., Jr.; Griffith, E. A. H.; Amma, E. L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 653).

[15] Packing forces must also be held accountable for at least some of the deformations. For example, the dihedral angle between the least-squares plane of ring 1 and the C(1)–C(2)–C(3) plane is 3.9°, and the tilt is away from C(2), but not toward C(3), as might have been expected.

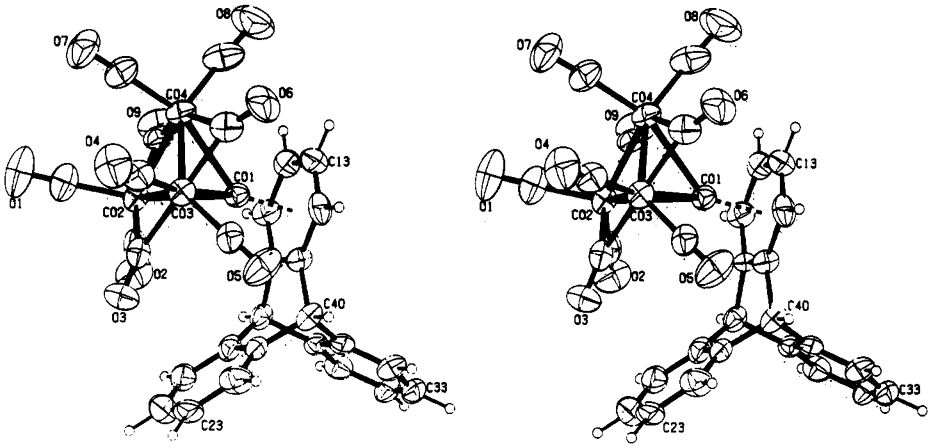

Figure 2. Stereoview of the X-ray structure of nonacarbonyl(η^6-triptycene)tetracobalt (2).

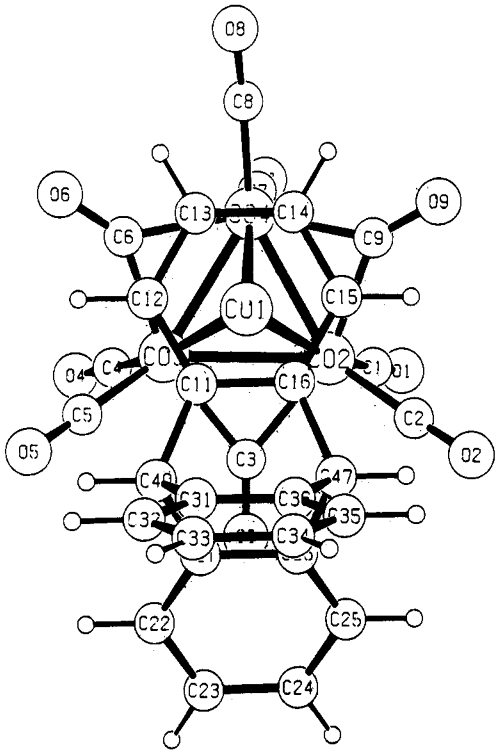

Figure 3. Projection of the structure of 2, viewed down the normal to the least-squares plane of arene ring 1.

Co(4), from the quasi-mirror plane, defined as for 1, are 0.009 and −0.031 Å, respectively; the two atoms thus lie roughly in the plane. The other two basal atoms, Co(2) and Co(3), straddle the plane, with perpendicular distances of −1.200 and 1.284 Å, respectively.

Comparisons with the structure of 1 and with the previously reported crystal structures of $Co_4(CO)_{12}$[16] and nonacarbonyl(η^6-benzene)tetracobalt (3)[17] reveal extensive similarities. As in 1, all three rings in 2 are closely approximated by regular hexagons; there is a slight pucker, with average deviations from the least-squares planes of 0.008, 0.003, and 0.005 Å for rings 1, 2, and 3, respectively.

Table IV. Final Atomic Parameters for 2[a]

atom	x	y	z	B_{eqv}, Å^2
Co(1)	0.40207 (4)	0.27834 (9)	0.59802 (11)	2.99 (8)
Co(2)	0.34636 (4)	0.20198 (9)	0.47118 (12)	3.21 (8)
Co(3)	0.33468 (5)	0.36225 (10)	0.53650 (12)	3.29 (8)
Co(4)	0.38965 (5)	0.32871 (10)	0.40368 (11)	3.60 (8)
O(1)	0.2889 (3)	0.1497 (5)	0.2841 (7)	7.4 (5)
O(2)	0.3578 (3)	0.0200 (5)	0.5724 (6)	5.8 (4)
O(3)	0.2749 (2)	0.2227 (4)	0.6147 (5)	4.5 (4)
O(4)	0.2644 (2)	0.4709 (5)	0.4303 (6)	6.6 (5)
O(5)	0.3287 (3)	0.4405 (5)	0.7547 (5)	6.0 (4)
O(6)	0.3971 (2)	0.5100 (5)	0.5104 (6)	5.6 (4)
O(7)	0.3412 (2)	0.3557 (5)	0.1939 (6)	6.5 (5)
O(8)	0.4753 (2)	0.3943 (6)	0.3544 (7)	8.1 (6)
O(9)	0.4254 (2)	0.1434 (5)	0.3701 (6)	5.7 (4)
C(1)	0.3101 (3)	0.1710 (7)	0.3565 (9)	4.8 (6)
C(2)	0.3530 (3)	0.0920 (7)	0.5346 (8)	4.0 (6)
C(3)	0.3034 (3)	0.2483 (7)	0.5677 (8)	3.6 (6)
C(4)	0.2912 (3)	0.4264 (7)	0.4680 (8)	4.4 (6)
C(5)	0.3305 (3)	0.4096 (6)	0.6687 (8)	3.7 (6)
C(6)	0.3807 (3)	0.4383 (7)	0.4944 (8)	4.0 (6)
C(7)	0.3600 (3)	0.3478 (7)	0.2736 (9)	4.6 (6)
C(8)	0.4415 (4)	0.3669 (8)	0.3708 (8)	5.6 (7)
C(9)	0.4005 (3)	0.1969 (7)	0.3988 (8)	4.2 (6)
C(11)	0.4128 (3)	0.2811 (7)	0.7771 (7)	2.8 (5)
C(12)	0.4330 (3)	0.3575 (6)	0.7279 (8)	3.6 (5)
C(13)	0.4611 (3)	0.3431 (8)	0.6431 (8)	4.5 (6)
C(14)	0.4691 (3)	0.2521 (8)	0.6051 (7)	3.9 (6)
C(15)	0.4483 (3)	0.1775 (6)	0.6525 (8)	3.7 (5)
C(16)	0.4214 (3)	0.1912 (6)	0.7391 (7)	2.6 (5)
C(21)	0.3468 (3)	0.2254 (7)	0.8606 (7)	3.2 (6)
C(22)	0.3060 (4)	0.2516 (7)	0.8862 (7)	4.6 (6)
C(23)	0.2720 (3)	0.1887 (10)	0.8725 (8)	4.7 (7)
C(24)	0.2800 (4)	0.1010 (9)	0.8329 (9)	5.4 (7)
C(25)	0.3210 (4)	0.0738 (7)	0.8068 (8)	4.4 (6)
C(26)	0.3544 (3)	0.1355 (8)	0.8215 (7)	3.3 (6)
C(31)	0.4160 (3)	0.2257 (7)	0.9622 (8)	2.9 (6)
C(32)	0.4321 (3)	0.2542 (7)	1.0640 (9)	4.0 (6)
C(33)	0.4566 (3)	0.1925 (9)	1.1286 (7)	4.2 (6)
C(34)	0.4651 (3)	0.1046 (8)	1.0917 (8)	4.2 (6)
C(35)	0.4486 (3)	0.0756 (6)	0.9897 (8)	3.6 (5)
C(36)	0.4239 (3)	0.1362 (7)	0.9257 (7)	2.7 (5)
C(40)	0.3875 (3)	0.2826 (6)	0.8805 (7)	3.0 (5)
C(47)	0.4028 (3)	0.1173 (6)	0.8109 (7)	3.1 (5)

[a] Standard deviations in parentheses. Parameters for hydrogen atoms and anisotropic thermal parameters are given in the supplementary material.

Also in common with 1, the average C–C distance in ring 1 (1.407 Å) of 2 is longer by ca. 0.02 Å than the corresponding distances in rings 2 (1.386 Å) and 3 (1.383 Å).[18] The average apical–basal Co–Co distance in 2 (2.500 Å) is significantly longer than the average basal–basal distance

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(16) Corradini, P. *J. Chem. Phys.* **1959**, *31*, 1676. Wei, C. H. *Inorg. Chem.* **1969**, *8*, 2384. Carré, F. H.; Cotton, F. A.; Frenz, B. A. *Ibid.* **1976**, *15*, 380. Data reported in the text for $Co_4(CO)_{12}$ are calculated from the atomic parameters listed by Wei.

(17) Bird, P. H.; Fraser, A. R. *J. Organomet. Chem.* **1974**, *73*, 103. Data reported in the text for 3 are taken from this reference or calculated from the atomic parameters listed in the Cambridge Crystallographic Database. The results for 3 "should probably be considered more reliable" than those for a disordered 1/1 mixture of (*o*-xylene)- and (*m*-xylene)nonacarbonyltetracobalt π complexes, whose crystal structure is described in the same paper.

(18) In 3, the average C–C distance in the benzene ring (1.39 Å) equals that in unperturbed benzene.[17]

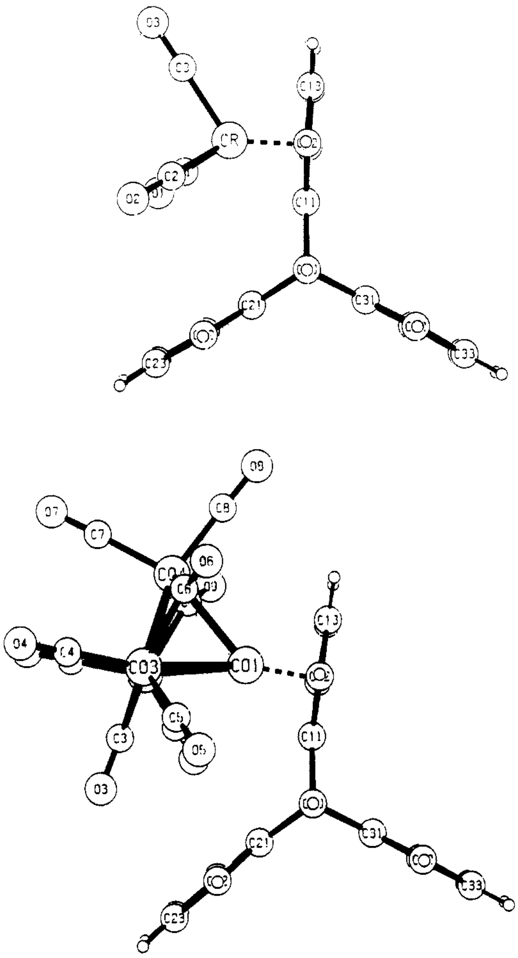

Figure 4. Projections of the structures of 1 (top) and 2 (bottom), viewed down the line connecting the triptycene bridgehead atoms, C(40)–C(47), in a direction normal to the quasi-mirror plane.

(2.462 Å), in line with a trend also found for $Co_4(CO)_{12}$ (2.494 and 2.484 Å) and for 3 (2.485 and 2.457 Å).[19] The average Co–C–O bond angles for terminal axial (176.6°) and terminal equatorial (177.6°) carbonyl groups in 2 are similar to the corresponding angles in 3 (177.3 and 178.5°, respectively). The Co_4 pyramids in $Co_4(CO)_{12}$, 2, and 3 are almost isometric. Thus, the perpendicular distances of the apical Co's from the basal planes are 2.039, 2.056, and 2.041 Å, respectively. The angles between the three planes that are perpendicular to the basal plane and to the three basal Co–Co bonds, and that pass through the apical Co atom, are 118.3, 120.0°, and 121.7° in $Co_4(CO)_{12}$ and 119.1, 120.1, and 120.8° in 2; in 3, which has crystallographic C_3 site symmetry, all three angles are 120.0°. In further similarity to 1 and 3, the carbon atoms in ring 1 of 2 are almost perfectly staggered with respect to the apical–basal Co–Co vectors (see Figure 3); the position of one of these vectors (Co(1)–Co(4)) in the quasi-mirror plane is analogous to the position of Cr–C(3) in 1.

There are, however, some other structural features that clearly differentiate 2 from 1, $Co_4(CO)_{12}$, and 3. To anticipate our conclusion, each of these features provides independent evidence for strong nonbonded interaction between the $Co_4(CO)_9$ fragment and ring 2. To begin with, consider the disposition of the apical cobalt atom relative to ring 1. Although the distance of Co(1) from the centroid of the ring (1.617 Å) is only slightly larger than that found for 3 (1.603 Å), the distances between the cobalt atom and the two C_{ar}'s in ring 1 of 2 that are closest to ring 2 (2.190 Å for Co(1)–C(11) and Co(1)–C(16)) are markedly longer than those between Co(1) and the other C_{ar}'s in ring 1 (2.139, 2.105, 2.112, and 2.128 Å for Co(1)–C(12), Co(1)–C(13), Co(1)–C(14), and Co(1)–C(15), respectively) and also longer than the corresponding distances in 3 (2.122 and 2.123 Å). The displacements here are considerably larger than the analogous Cr–C_{ar} displacements in 1, discussed above.

Furthermore, the triptycene framework is significantly deformed in such a way as to spread apart rings 1 and 2, evidently to accommodate the bulky $Co_4(CO)_9$ fragment. First, as in 1, closure of the C(11)–C(40)–C(31) and C(16)–C(47)–C(36) angles to 103.5° is accompanied by a concomitant opening of the other four C–C–C angles subtended at the bridgehead atoms; but now, in contrast to 1, the pair that relates rings 1 and 2, C(11)–C(40)–C(21) and C(16)–C(47)–C(26), opens to 109.1°, while the remaining pair, which relates rings 2 and 3, retains a value (105.2°) close to that found for triptycene itself. As a result, the dihedral angle between least-squares planes 1A (C(40)–C(11)–C(16)–C(47)) and 2A (C(40)–C(21)–C(26)–C(47)) has opened to 124.1°, while the corresponding angles between planes 1A and 3A (C(40)–C(31)–C(36)–C(47)) and between planes 2A and 3A are 117.0° and 118.9°, respectively. Second, the least-squares planes of rings 1 and 2 are bent away from 1A and 2A by 8.7° and 5.8°, respectively, both in the direction of ring 3, while the plane of ring 3 barely deviates from 3A (0.7°). The effect is plainly visible in the projection diagram of Figure 4.

In addition, the angle between the basal plane of the three cobalt atoms and the least-squares plane of ring 1 is 8.3°, the result of tilting the $Co_4(CO)_9$ fragment away from ring 2 (see Figure 4). But perhaps the most curious manifestation of repulsive nonbonded interaction between the $Co_4(CO)_9$ fragment and ring 2 is provided by the spatial disposition of C(3)–O(3), the bridging carbonyl group that points toward ring 2. If we define ϕ as the dihedral angle between the basal Co_3 plane and the plane formed by two basal atoms and a bridging carbonyl carbon atom, then in 3 $\phi = 11.9°$, in $Co_4(CO)_{12}$ $\phi = 3.4$, 6.1, and 5.3°, and in 2 $\phi = 17.5°$ for C(9), 15.0° for C(6), but −4.1° for C(3). That is, C(3) in 2 points *away* from Co(1), whereas all the other bridging carbonyl carbons point *toward* the apical cobalt atom.

Finally, returning to the very beginning of our discussion, there now seems little doubt that the strongly perturbed (to judge by the ^1H NMR spectrum) uncomplexed ring in 2 is identified as ring 2.

The foregoing comparisons between 1 and 2 clearly establish that the effect of nonbonded repulsions on the ground-state structure of triptycene transition-metal π complexes is far greater for the sterically demanding tripod ligand $Co_4(CO)_9$ than for $Cr(CO)_3$. It remains to be seen how this effect is expressed in the internal dynamics of molecules such as 1 and 2.

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Registry No. 1, 73016-86-1; 2, 98104-70-2; $Co_4(CO)_{12}$, 17786-31-1; triptycene, 477-75-8.

Supplementary Material Available: Tables of bond lengths and bond angles in 2 (Tables V and VI), final atomic parameters for hydrogen atoms (Tables VII and VIII), anisotropic thermal parameters (Tables IX and X), and structure factor tables for 1 and 2 (Tables XI and XII) (43 pages). Ordering information is given on any current masthead page.

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[19] In light of this finding, the conclusion by Bird and Fraser[17] that the average basal–basal Co–Co distance "differs little" from the average apical–basal distance, and that, in general, "the presence of a bridging carbonyl has little effect on the cobalt–cobalt bond length" deserves reexamination.