Under these conditions, less than 1% of the 1-hexene solvent was converted to *n*-hexane in a 24-h period at 25 °C.

Hydrogen reacted with a benzene solution of $(\eta^3\text{-}C_3H_5)Ir(\eta^4\text{-COD})[P(OCH_3)_3]$ to form propane, cyclooctane, and a new iridium complex. The ^1H NMR spectrum of this hydride consisted of a phosphite methoxy doublet resonance and a broad complex multiplet in the hydride region. All attempts to isolate the hydride in crystalline form failed; the hydride appeared to be a multinuclear iridium hydride, possibly analogous to the $[HRhP(OR)_3]_x$[4] complexes.

Both $(\eta^3\text{-}C_3H_5)Ir[P(OCH_3)_3]_3$ and $(\eta^3\text{-}C_3H_5)Ir(\eta^4\text{-1,5-COD})[P(OCH_3)_3]$ were active catalyst precursors for 1-hexene hydrogenation to hexane (Table I). Isomerization of the 1-hexene to the *cis*- and *trans*-2-hexene and *cis*- and *trans*-3-hexene isomers was a significant (~10%) competing process to olefin hydrogenation with the latter complex but not with the former (<1% isomerization). The mixture of $(\eta^3\text{-}C_3H_5)Ir[P(OCH_3)_3]_3$–hydrogen cleavage products also catalyzed 1-hexene hydrogenation and isomerization. In separate experiments with the hydrides derived from the allyliridium complex, it was established that the $H_3Ir[P(OCH_3)_3]_3$ isomers are active species in the reaction system. However, the catalytic activity of the trihydrides was lower than for the parent allyl complex, and these trihydrides, unlike the allyl precursor complex, were, in the presence of hydrogen, active olefin isomerization catalysts. $HIr[P(OCH_3)_3]_4$, like the cobalt[2] analogue, was not detectably active as a catalyst for olefin hydrogenation.

Generally, the presence of a reducible substrate like 1-hexene appeared to "inhibit" the reductive hydrogenation of the organic ligands in the allyliridium complexes. As noted above, $(\eta^1\text{-}C_3H_5)Ir(\eta^4\text{-1,5-COD})[P(OCH_3)_3]_2$ was not an active catalyst for either olefin isomerization or hydrogenation. The presence of 1-hexene literally blocked (over a 24-h reaction period) the hydrogenation of the allyl and cyclooctadiene ligands in the bis(phosphite) complex, whereas this process was relatively fast in the absence of an olefin (benzene solution). Presumably, the hexene captured a coordinately unsaturated intermediate, an intermediate that reacts with hydrogen to effect, ultimately, the hydrogenation of the hydrocarbon ligands. The effect of the presence of a reducible substrate on the rate of allyl–metal bond cleavage was also observed for (trialkyl phosphite)allylcobalt complexes; the rate was substantially higher in cyclohexane solution than in benzene (a reducible substrate for these cobalt complexes).[3,6,10]

Acknowledgment. This research was supported by the National Science Foundation and by a generous loan of iridium chloride by Johnson Matthey, Inc. A. C. Sievert and R. R. Burch assisted in the NMR measurements. NMR measurements at 360 MHz were performed at the Stanford Magnetic Resonance Laboratory with support from NSF Grant no. GP23633 and NIH Grant No. RR00711. V.W.D. acknowledges the Camille and Henry Dreyfus Foundation for support in the form of a Teacher-Scholar Award.

Registry No. 4, 82932-72-7; $(\eta^1\text{-}C_3H_5)Ir(COD)[P(OCH_3)_3]_2$, 82932-73-8; $(\eta^3\text{-}C_3H_5)IR[P(OCH_3)_3]_3$, 82951-07-3; $HIr[P(OCH_3)_3]_4$, 82932-74-9; *lac*-$H_3Ir[P(OCH_3)_3]_3$, 82932-75-0; *mer*-$H_3Ir[P(OCH_3)_3]_3$, 82977-26-2; 1-hexene, 592-41-6.

Supplementary Material Available: Crystal structure analysis report, structure factor amplitude table, and Tables III, IV, and VI for anisotropic thermal parameters, idealized atomic coordinates for hydrogen atoms, and ligand bond lengths and angles, respectively, in 4 (22 pages). Ordering information is given on any current masthead page.

Formation and Molecular Structure of (η^4-Tetraphenylcyclobutadiene)dicarbonylnitrosylmanganese†

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A reaction between tetracarbonylnitrosylmanganese and diphenylacetylene in refluxing toluene solution has produced the title compound, $[\eta^4\text{-}(C_6H_5)_4C_4](CO)_2(NO)Mn$, in low yield. The product, which represents the first cyclobutadiene derivative of a group 7B metal, has been characterized by infrared and mass spectral data as well as by a single-crystal X-ray diffraction study. $[\eta^4\text{-}(C_6H_5)_4C_4](CO)_2(NO)Mn$ crystallizes in the monoclinic space group $P2_1/c$ with lattice parameters $a = 8.921$ (2) Å, $b = 18.775$ (8) Å, $c = 14.056$ (5) Å, $\beta = 92.27$ (3)°, and $D_{calcd} = 1.40$ g cm^{-3} for $Z = 4$. Least-squares refinement gave a final R value of 0.041 using 878 independent observed reflections. The tetraphenylcyclobutadiene ligand is η^4 coordinated to the Mn atom at an average Mn–C distance of 2.11 (2) Å. The four atoms of the cyclobutadiene ring are planar to within 0.001 Å. Two of the X–O (X = N or C) ligands are disordered.

Introduction

The formation, structure, and properties of cyclobutadiene have fascinated both synthetic and theoretical chemists for over a century.[2] In recent years, organometallic chemistry has played a significant role in the development of this topic. Thus, while cyclobutadiene itself is highly unstable, Longuet-Higgins and Orgel[3] proposed in 1956 that cyclobutadiene might form stable

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† Dedicated to the late Professor Rowland Pettit, a brilliant and dedicated chemist whose enthusiasm for research was equaled only by his friendship for his fellow colleagues.

(1) (a) University of Massachusetts. (b) University of Alabama.
(2) Maier, G. *Angew. Chem., Int. Ed. Engl.* 1974, *13*, 425.
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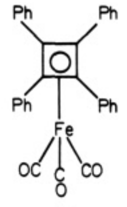
complexes with transition metals, and soon thereafter Hübel and Braye[4] as well as Criegee and Schröder[5] reported the successful isolation of the stable organometallic compounds (η^4-tetraphenylcyclobutadiene)tricarbonyliron (**1**) and the dimeric (η^4-tetramethylcyclobutadiene)dichloronickel (**2**), respectively. The first transition-metal complex of the parent hydrocarbon, viz., (η^4-cyclobutadiene)tricarbonyliron (**3**), was prepared by Pettit and co-workers in 1965.[6]



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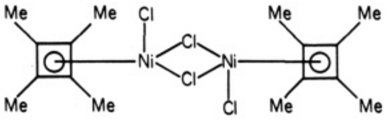

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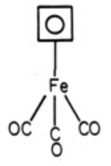

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Since that time, a large number of new (cyclobutadiene)metal compounds have been isolated, and their structures and reactivities have been extensively investigated.[7] It is notable, however, that there are presently no reported group 7B (cyclobutadiene)metal compounds, even though stable cyclobutadiene derivatives are now known for every other transition-metal triad.

In this article, we describe the synthesis and molecular structure of (η^4-tetraphenylcyclobutadiene)dicarbonylnitrosylmanganese (**5**), the first cyclobutadiene complex of a group 7B metal. It is appropriate that these results be published in this special issue of *Organometallics* dedicated to the late Professor Rowland Pettit, in view of his many pioneering, significant, and imaginative contributions to (cyclobutadiene)metal chemistry.[8] With the isolation and structural elucidation of the (cyclobutadiene)manganese complex **5**, the series of known cyclobutadiene derivatives of the transition metals from group 4B through group 8 is now complete.

Results and Discussion

Since pentacarbonyliron, $Fe(CO)_5$, has played a key role in the formation of (cyclobutadiene)metal compounds,[7] it seemed possible that the isoelectronic manganese analogue, tetracarbonylnitrosylmanganese (**4**), might also serve as a useful precursor for (cyclobutadiene)manganese compounds. The substitution of a carbonyl ligand in **4** by nucleophiles such as phosphines and phosphites has been examined under both thermal[9] and photochemical[10] conditions. Moreover, irradiation of **4** in the presence of 1,3-butadiene has yielded the carbonyl substitution product $(\eta^4\text{-}C_4H_6)(CO)_2(NO)Mn$ as well as a paramagnetic 17-electron complex $(\eta^4\text{-}C_4H_6)_2(CO)Mn$, whose structure has been confirmed by X-ray crystallography.[11,12]

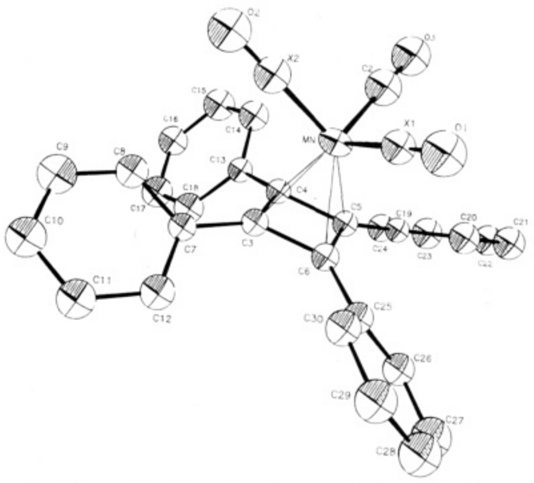
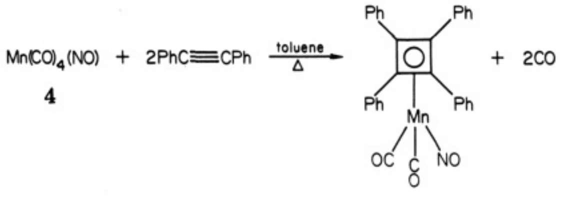


Figure 1. The molecular structure and atom labeling scheme for $[\eta^4\text{-}(C_6H_5)_4C_4](CO)_2(NO)Mn$. The atoms are represented by their 50% probability ellipsoids for thermal motion.

We therefore decided to investigate a possible reaction between **4** and diphenylacetylene, since cyclodimerization of this acetylene to form (η^4-tetraphenylcyclobutadiene)metal compounds is well-known and fairly general in scope.[7] Photolysis of a benzene solution of diphenylacetylene and **4** did not lead to any identifiable products. However, a thermal reaction between **4** and diphenylacetylene in refluxing toluene resulted in the formation of an air-stable, orange crystalline compound in low yield.



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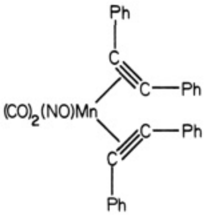
Elemental and mass spectral analyses (M^+ 498) of the resulting reaction product were consistent with a molecular formula $[(C_6H_5)_4C_4](CO)_2(NO)Mn$. An IR spectrum of the product in toluene solution exhibited carbonyl stretching frequencies at 2010 and 1970 cm^{-1}, as well as a nitrosyl stretching frequency at 1720 cm^{-1}. The IR spectrum in KBr was very similar to that reported previously for **1**.[13]

While the above data are consistent with a formulation of the reaction product as the η^4-tetraphenylcyclobutadiene complex **5**, they do not rule out a metallacyclic structure (**6**) or a bis(η^2-diphenylacetylene) structure (**7**) as possibilities. In view of the air stability and high thermal stability of the reaction product, as well as the tendency of manganese to invariably form 18- rather than 16-electron organometallic complexes, structure **7** seemed highly



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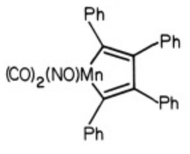

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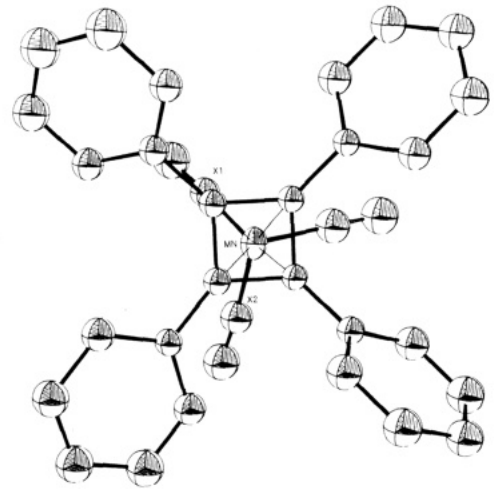

Figure 2. View of $[\eta^4\text{-}(C_6H_5)_4C_4](CO)_2(NO)Mn$ normal to the butadiene plane.

unlikely. Further, the relative stability of the product as well as the apparent lack of coordinated acetylenic frequencies in the IR spectrum would also appear to favor structure 5 over 6, although the latter frequencies could conceivably not be observable, due to overlap with the intense carbonyl and nitrosyl bands.

For the structure of the reaction product to be unambiguously determined, a single-crystal X-ray diffraction study was therefore undertaken. The molecular structure and atom numbering scheme are presented in Figure 1. The compound is isostructural with $[\eta^4\text{-}(C_6H_5)_4C_4](CO)_3Fe$ (1).[14] The cyclobutadiene ligand is symmetrically bound to the manganese atom at an average Mn–C(η^4) distance of 2.11 (2) Å. Although the molecule exhibits no crystallographically imposed symmetry, the four-membered carbocyclic ring is planar to better than 0.001 Å.

Few details of the bonding of the dicarbonyl nitrosyl tripod to the metal bear discussion because of the disorder problem. However, it is noteworthy that one of the X–O groups (X = N or C) is eclipsed by a Mn–C(η^4) bond, while the other two X–O moieties are bisected by another Mn–C(η^4) bond. This is shown clearly in Figure 2. A manifestation of this is that the phenyl group "trans" to the eclipsed Mn-XO bond is twisted far more out of the butadiene plane than are the other three. The dihedral angles are 27, 33, and 37° for the latter vs. 60° for the former. A related observation (also noted in the structure of 1)[14] is that the carbon atom of the large-twist phenyl group lies 18° out of the C_4 plane, compared with 9° for the other three. This feature was attributed to packing effects in the discussion of 1 but may well be electronic in origin. Of the other transition-metal structures containing an $[\eta^4\text{-}(C_6H_5)_4C_4]$ ligand,[15-20] no consistent pattern has yet emerged for the bend and twist of the phenyl substituents from the C_4 plane. In $(\eta^5\text{-}C_5H_5)[\eta^4\text{-}(C_6H_5)_4C_4]Rh$,[15] the phenyl groups are bent away from the metal at a mean angle of 7° with angles of twist ranging from 32 to 43°. Much larger perturbations have been noted in $[\eta^4\text{-}(C_6H_5)_4C_4]_2(CO)_2Mo$,[16] where the angles of twist ranged from 31 to 84°.

Table I. Bond Distances (Å) and Angles (deg) for $[\eta^4\text{-}(C_6H_5)_4C_4](CO)_2(NO)Mn$

Bond Distances

Mn–X(1)	1.72 (1)	Mn–X(2)	1.78 (1)
Mn–C(2)	1.84 (1)	Mn–C(3)	2.12 (1)
Mn–C(4)	2.084 (9)	Mn–C(5)	2.10 (1)
Mn–C(6)	2.13 (1)	O(1)–X(1)	1.16 (1)
O(2)–X(2)	1.16 (1)	O(3)–C(2)	1.14 (1)
C(3)–C(4)	1.45 (1)	C(3)–C(6)	1.46 (1)
C(3)–C(7)	1.45 (1)	C(4)–C(5)	1.46 (1)
C(4)–C(13)	1.46 (1)	C(5)–C(6)	1.47 (1)
C(5)–C(19)	1.46 (1)	C(6)–C(25)	1.47 (1)
C(7)–C(8)	1.39 (1)	C(7)–C(12)	1.41 (1)
Cent–Mn	1.836		

Bond Angles

X(1)–Mn–X(2)	99.4 (5)	X(1)–Mn–C(2)	100.5 (5)
X(2)–Mn–C(2)	98.8 (5)	Mn–X(1)–O(1)	176.9 (9)
Mn–X(2)–O(2)	176 (1)	Mn–C(2)–O(3)	179 (1)
Mn–C(3)–C(6)	70.1 (6)	C(4)–C(3)–C(6)	89.9 (8)
C(4)–C(3)–C(7)	131.8 (9)	C(6)–C(3)–C(7)	137.4 (9)
C(3)–C(4)–C(5)	90.8 (8)	C(3)–C(4)–C(13)	130 (1)
C(5)–C(4)–C(13)	134 (1)	C(4)–C(5)–C(6)	89.1 (8)
C(4)–C(5)–C(19)	132.4 (9)	C(6)–C(5)–C(19)	137.5 (9)
C(3)–C(6)–C(5)	90.2 (8)	C(3)–C(6)–C(25)	134 (1)
C(5)–C(6)–C(25)	134.2 (9)	C(3)–C(7)–C(8)	120.5 (9)
X(1)–Mn–Cent	120.26	X(2)–Mn–Cent	119.61
C(2)–Mn–Cent	114.49		

Experimental Section

All reactions, manipulations, and crystallizations were conducted under an atmosphere of dry argon by using standard Schlenk and cannula techniques. Toluene, hexane, and methylene chloride were dried over calcium hydride and freshly distilled from calcium hydride under argon before use. IR spectra were obtained on a Perkin-Elmer 237-B spectrometer and were calibrated vs. polystyrene. Mass spectra were obtained on a Perkin-Elmer-Hitachi RMU-6L instrument at 70 eV. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Diphenylacetylene was prepared according to a literature procedure.[21] Tetracarbonylnitrosylmanganese was best synthesized from pentacarbonylhydridomanganese and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide[22,23] and was purified by vacuum line manipulations.

Preparation of (η^4-Tetraphenylcyclobutadiene)dicarbonylnitrosylmanganese. A 100-mL Schlenk flask was flushed well with argon and was charged with 1.18 g (6.62 mmol) of diphenylacetylene, 0.65 g (3.3 mmol) of freshly distilled tetracarbonylnitrosylmanganese, and 50 mL of toluene. The flask was equipped with a reflux condenser and the solution heated at reflux for 12 h. After cooling, ca. 2 g of alumina was added to the reaction mixture, the solvent was evaporated under vacuum, and the residue was placed onto a 2 × 36 cm alumina column (CAMAG neutral grade, deactivated with 5% by weight of argon-saturated water). Elution with hexane produced a rapidly moving yellow band which was collected. IR analysis of this band indicated the presence of $Mn_2(CO)_{10}$. Elution with hexane was continued until ca. 150 mL of eluent had been collected. The fractions were combined, the solvent was removed under reduced pressure, and the resulting light yellow crystals were placed in a sublimer. The apparatus was evacuated (ca. 10^{-2} mmHg) and then slowly warmed to 60 °C, while the water-cooled probe was left at room temperature. In this way, the yellow $Mn_2(CO)_{10}$ was sublimed. The water to the cold finger was next turned on, and sublimation was continued, producing 1.10 g (93% recovery) of

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Table II. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	$[\eta^4\text{-}(C_6H_5)_4C_4](CO)_2(NO)Mn$
mol wt	497.4
space group	$P2_1/c$
cell constants	
a, Å	8.921 (2)
b, Å	18.775 (8)
c, Å	14.056 (5)
β, deg	92.27 (3)
cell vol, Å^3	2352.4
molecules/unit cell	4
D_{calcd}, g cm^{-3}	1.40
μ_{calcd}, cm^{-1}	6.23
radiatn	Mo Kα
max cryst dimens, mm	0.25 × 0.50 × 0.50
scan width	0.80 + 0.20 tan *θ*
std reflctns	(060), (006)
decay of stds	±2%
reflctns measd	1902
2*θ* range, deg	36
reflctns collected	878
no. of parameters varied	146
GOF	2.53
R	0.041
R_w	0.048

diphenylacetylene. Subsequent elution of the column with 1:1 hexane–toluene developed an orange band which was collected, and the solvent was removed under vacuum, leaving 81 mg (5%) of orange (η^4-tetraphenylcyclobutadiene)dicarbonylnitrosylmanganese. An analytical sample was obtained by recrystallization from methylene chloride–hexane at −20 °C: mp 192 °C dec; IR (KBr) 3050 (w), 3025 (sh), 2010 (vs), 1975 (vs), 1930 (s), 1820 (vw), 1760 (sh), 1730 (vs), 1595 (m), 1495 (s), 1440 (vw), 1435 (vw), 1385 (w), 1375 (w), 1300 (vw), 1250 (vw), 1170 (w), 1140 (w), 1085 (br w), 1060 (m), 1015 (m), 940 (vw), 900 (vw), 770 (m), 760 (sh), 740 (m), 730 (m), 685 (s) cm^{-1}; IR (toluene) ν_{CO} 2010, 1970 cm^{-1}, ν_{NO} 1720 cm^{-1}; mass spectrum, *m/e* 498 (M$^+$).

Anal. Calcd for $C_{30}H_{20}MnNO_3$: C, 72.44; H, 4.05; N, 2.82. Found: C, 72.22; H, 4.02; N, 2.80.

X-ray Data Collection, Structure Determination, and Refinement. Single crystals suitable for X-ray diffraction studies were grown by carefully layering hexane onto a solution of (η^4-tetraphenylcyclobutadiene)dicarbonylnitrosylmanganese (**5**) in methylene chloride. The resulting mixture was allowed to stand undisturbed for ca. 72 h, during which time diffusional mixing of the two layers had occurred, effecting the formation of orange crystals. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($\theta >$ 15°) accurately centered on the diffractometer are given in Table II. The space group was uniquely determined as $P2_1/c$ from the systematic absences in $0k0$ for $k = 2n + 1$ and in $h0l$ for $l = 2n + 1$.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. The method has been previously described.[24] A summary of data collection parameters is given in Table II. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Calculations were carried out with the SHELX system of computer programs.[25] Neutral atom scattering factors for Mn, O, N, and C were taken from Cromer and Waber,[26] and the scattering for manganese was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.[27] Scattering factors for H were from ref 28.

The position of the manganese atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the manganese atom readily revealed the position of the non-hydrogen atoms. In locating the nitrogen atom, it became evident that some disorder was present. Initially all three atoms of the X–O ligands (X = N or C) were treated as carbon atoms. Two of the X–O positions refined with very low-temperature factors (one of which was negative). The third position showed no signs of disorder, and its Mn–X bond length was significantly greater than the other two. At this point it was clear that the N–O ligand was disordered over two of the X–O positions. X(1) and X(2) were thus refined as mixtures of 50% N and 50% C. Other ratios were tried, but no significant change in the *R* values was observed. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.058$. The hydrogen atoms of the phenyl rings were placed at calculated positions 1.08 Å from the bonded carbon atom and were not refined. Refinement of the manganese atom with anisotropic temperature factors led to final values of $R = 0.041$ and $R_w = 0.048$. A final difference Fourier showed no feature greater than 0.3 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the

Table III. Final Fractional Coordinates for $[\eta^4\text{-}(C_6H_5)_4C_4](CO)_2(NO)Mn$

atom	*x/a*	*y/b*	*z/c*
Mn	1.0992 (2)	0.3050 (1)	0.4863 (1)
O(1)	1.378 (1)	0.2406 (5)	0.4378 (6)
O(2)	1.1804 (9)	0.4546 (5)	0.4536 (6)
O(3)	0.908 (1)	0.2766 (4)	0.3120 (6)
X(1)	1.265 (1)	0.2667 (5)	0.4547 (7)
X(2)	1.143 (1)	0.3959 (6)	0.4651 (7)
C(2)	0.982 (1)	0.2877 (6)	0.3785 (9)
C(3)	1.064 (1)	0.3222 (5)	0.6328 (7)
C(4)	0.923 (1)	0.3111 (6)	0.5790 (7)
C(5)	0.962 (1)	0.2366 (5)	0.5627 (7)
C(6)	1.104 (1)	0.2481 (5)	0.6171 (7)
C(7)	1.119 (1)	0.3814 (6)	0.6906 (7)
C(8)	1.072 (1)	0.4505 (6)	0.6698 (8)
C(9)	1.120 (1)	0.5076 (6)	0.7253 (9)
C(10)	1.216 (1)	0.4969 (7)	0.8052 (9)
C(11)	1.259 (1)	0.4293 (6)	0.8297 (8)
C(12)	1.213 (1)	0.3701 (6)	0.7718 (8)
C(13)	0.781 (1)	0.3496 (6)	0.5830 (8)
C(14)	0.687 (1)	0.3674 (6)	0.5021 (8)
C(15)	0.552 (1)	0.4022 (6)	0.5139 (9)
C(16)	0.502 (1)	0.4207 (6)	0.6019 (8)
C(17)	0.591 (1)	0.4041 (6)	0.6817 (8)
C(18)	0.729 (1)	0.3693 (6)	0.6718 (8)
C(19)	0.876 (1)	0.1764 (5)	0.5247 (7)
C(20)	0.947 (1)	0.1192 (6)	0.4809 (8)
C(21)	0.863 (1)	0.0615 (6)	0.4441 (8)
C(22)	0.709 (1)	0.0602 (6)	0.4495 (8)
C(23)	0.639 (1)	0.1163 (6)	0.4930 (8)
C(24)	0.720 (1)	0.1749 (6)	0.5303 (7)
C(25)	1.222 (1)	0.2007 (6)	0.6569 (7)
C(26)	1.181 (1)	0.1325 (6)	0.6823 (8)
C(27)	1.288 (1)	0.0852 (7)	0.7279 (9)
C(28)	1.429 (1)	0.1102 (7)	0.7448 (9)
C(29)	1.474 (1)	0.1773 (6)	0.7202 (8)
C(30)	1.368 (1)	0.2245 (6)	0.6748 (8)
H(1)[C(8)]	1.0006	0.4611	0.6095
H(2)[C(9)]	1.0834	0.5585	0.7098
H(3)[C(10)]	1.2526	0.5414	0.8451
H(4)[C(11)]	1.3257	0.4216	0.8900
H(5)[C(12)]	1.2519	0.3195	0.7883
H(6)[C(14)]	0.7213	0.3548	0.4355
H(7)[C(15)]	0.4830	0.4140	0.4541
H(8)[C(16)]	0.3977	0.4465	0.6092
H(9)[C(17)]	0.5573	0.4174	0.7502
H(10)[C(18)]	0.7940	0.3586	0.7322
H(11)[C(20)]	1.0631	0.1199	0.4769
H(12)[C(21)]	0.9183	0.0202	0.4121
H(13)[C(22)]	0.6454	0.0175	0.4194
H(14)[C(23)]	0.5240	0.1146	0.4993
H(15)[C(24)]	0.6618	0.2167	0.5626
H(16)[C(26)]	1.0712	0.1129	0.6696
H(17)[C(27)]	1.2566	0.0348	0.7518
H(18)[C(28)]	1.5116	0.0753	0.7742
H(19)[C(29)]	1.5803	0.1953	0.7376
H(20)[C(30)]	1.4011	0.2748	0.6532

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positional and thermal parameters are given in Table III.[29]

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Supplementary Material Available: Tables of thermal parameters, least-squares plane results, phenyl ring bond distances (Å) and angles (deg), and observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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[29] See paragraph at the end of paper regarding supplementary material.

Synthesis, Crystal and Molecular Structure, and Chemistry of (μ-Trimethylene)bis(η-cyclopentadienyl)bis(μ-carbonyl)dicobalt, a Five-Membered Dicobaltacycle†

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Treatment of $Na[CpCo(CO)]_2$ with 1,*n*-dihaloalkanes leads in certain cases to double alkylation, giving dinuclear metallacycles containing two adjacent cobalt atoms. This paper reports the synthesis and study of several such systems and an in-depth investigation of the five-membered dimetallacycle **1** prepared from 1,3-diiodopropane. The molecular structure of **1** was determined by X-ray diffraction, using 1016 reflections (R = 2.47). The crystals were orthorhombic (space group *Fdd*2), with unit-cell parameters a = 16.7983 Å, b = 45.576 Å, c = 6.9565 Å. The complex has an "open envelope" ring structure, with a dihedral angle of 32.9°; the Co–Co bond distance is 2.413 Å. Thermolysis of **1** (80–100°) gives cyclopropane and propene. Reaction of **1** with CO or phosphines (L) occurs at lower temperature, leading to a product distribution which is dependent upon the concentration of L. At low [L], the reaction leads to cyclopropane mixed with a small amount of propene and CpCo(L)(CO). High [L] produces CpCo(L)(CO) and mononuclear metallacyclopentanones **6**, **7**, or **8** depending on the entering ligand. Thermolysis of the metallacyclopentanones leads again to cyclopropane and propene rather than to cyclobutanone. Kinetic and isotope labeling studies on the reaction of **1** with dative ligands suggest a mechanism involving initial formation of dicobaltacyclohexanones A and B. B then is postulated to rearrange to a mononuclear carbonylmetallacyclobutane complex (C) which can either eliminate C_3 hydrocarbons or undergo CO insertion, leading to metallacyclopentanone.

Introduction

Metallacycles—heterocycles containing a transition metal in the ring—have been a subject of intensive study by organometallic chemists. The longest known members of this class of complexes are the carbon-unsaturated "metalloles" formed during metal-induced oligomerization or cyclotrimerization of acetylenes.[1,2] More recently, carbon-saturated metallacycles have been implicated in important processes such as C–H activation,[3] olefin metathesis,[4] alkene dimerization,[5] and metal-catalyzed isomerization of organic small-ring compounds.[6] The synthesis of stable, isolable members of this class of complexes has helped in elucidating their properties and understanding the role they play in the processes mentioned above.

There is increasing evidence that many metal-mediated processes depend on catalysts or intermediates containing more than one metal.[7] Despite this, the majority of metallacycles studied so far contain only one metal in the ring. An interesting departure from this trend is the provocative series of carbon-unsaturated metallacycles formed by sequential insertion of alkynes into a dinuclear molybdenum system[8] and the class of dimetallacyclopropanes (μ-methylene complexes) which have been prepared and studied recently.[9]

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† This paper is submitted in memory of Rowland Pettit, a brilliant chemist and good friend. We have chosen this manuscript because of the interest we shared in the chemistry of dinuclear metallacycles, but we hope it will serve as our tribute to Pettit's many important contributions to organotransition-metal chemistry from its early days to the most recent times.

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