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A potassium cryptate-2,2,2 salt of tricarbonyl(η^4-cyclopentadiene)manganese

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Key indicators

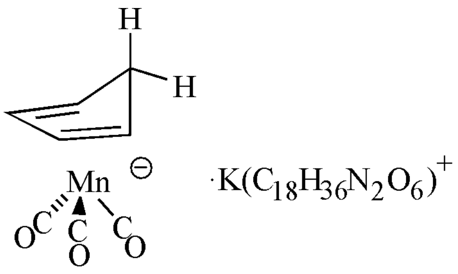
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.101
Data-to-parameter ratio = 26.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Use of $[Mn(\eta^4\text{-}C_6H_6)(CO)_3]^-$ prepared by anthracenide reduction of $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]PF_6$ provides access to the title compound, (4,7,13,16,21,24-hexaoxa-1,l0-diazabicyclo[8.8.8]hexacosane)potassium tricarbonyl(cyclopentadiene)manganate(I), $[K(C_{18}H_{36}N_2O_6)][Mn(C_5H_6)(CO)_3]$, by reaction of $[Mn(\eta^4\text{-}C_6H_6)(CO)_3]^-$ with excess of the cyclopentadiene monomer (C_5H_6) at 195 K. In the title compound, there is octacoordination of potassium by two N and six O atoms of the 4,7,13,16,21,24-hexaoxa-1,l0-diazabicyclo[8.8.8]-hexacosane and η^4-coordination of the diene in an envelope conformation to the $Mn(CO)_3^-$ center, with the methylene group folded out of the coordination plane.

Comment

We have previously reported that the η^4-benzene ligand in $[Mn(\eta^4\text{-}C_6H_6)(CO)_3]^-$ is activated with respect to substitution of the η^4-benzene by polyaromatic hydrocarbons to give products such as the η^4-naphthalene complex $[Mn(\eta^4\text{-}C_{10}H_8)(CO)_3]^-$ (Thompson *et al.*, 1991). η^4-Benzene substitution by anthracene is much slower than substitution by naphthalene (Lee *et al.*, 1995), and $[Mn(\eta^4\text{-}C_6H_6)(CO)_3]^-$ prepared by anthracenide reduction can, therefore, provide access to the title compound, (4,7,13,16,21,24-hexaoxa-1,l0-diazabicyclo[8.8.8]hexacosane)potassium tricarbonyl(cyclopentadiene)manganate(I), by competitive substitution with excess cyclopentadiene monomer (C_5H_6). To the best of our knowledge, while there are several crystal structures of η^4-complexes of heterosubstituted cyclic dienes with manganese(I) (Lindner *et al.*, 1979, 1981*a*,*b*, 1988, 1996; Chen *et al.*, 1996), the title compound, (I), is the first crystallographically characterized $[Mn(\eta^4\text{-diene})(CO)_3]^-$ complex of an aliphatic diene (Fig. 1), although a methyl-substituted analog has been spectroscopically characterized prior to this study (Lee & Cooper, 1991).



(I)

The C_5H_6 ligand coordinated to $Mn(CO)_3^-$ has an envelope conformation (Duax *et al.*, 1976) with the CH_2 bent out of the plane by 34.6 (1)°. There is a non-crystallographic plane of symmetry that includes the CH_2 group and the Mn center. This contrasts sharply with the structure of uncoordinated C_5H_6 (Liebling & Marsh, 1965), in which the C_5H_6 ring is almost planar but lacks a plane of symmetry that would render the methylene H atoms equivalent.

Experimental

Reactions and manipulations were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk and cannula techniques or a dry box. A 0.2 *M* potassium anthracenide/THF solution (7.3 ml, 1.46 mmol, 2.1 equivalents per Mn metal) was added to a slurry of 0.25 g (0.69 mmol) $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]PF_6$ in 15 ml THF at 195 K to form a yellow–green slurry. After 15 min, excess distilled cyclopentadiene C_5H_6 monomer (2.0 ml) was added to the stirred solution to give a yellow slurry. The yellow solution was collected by filtration at 195 K and mixed with 0.21 g (0.56 mmol) 4,7,13,16,21,24-hexaoxa-1,l0-diazabicyclo[8.8.8]hexacosane. Solvent THF was removed under vacuum at ambient temperature, and the residue rinsed with pentane (50 ml) and toluene (50 ml), and then redissolved in a small amount of DME and layered with Et_2O, to give orange crystals suitable for diffraction studies (0.26 g, yield 41%) at 243 K. IR absorptions for the title compound [ν_{co} only, THF, 1925 (*s*), 1830 (*s*), 1811(*s*) cm^{-1}] are in the same range as those of $[Mn(\eta^4\text{-cyclohexadiene})(CO)_3]^-$ (Brookhart *et al.*, 1983) and $[Mn(\eta^4\text{-butadiene})(CO)_3]^-$ (Brookhart *et al.*, 1987), while the ^1H NMR spectrum of (I) has three peaks [in CD_3CN, 273 K, δ 5.0 (*s*, 2 CH), 2.70 (*s*, 2 CH), 1.86 (*s*, CH_2)] for the C_5H_6 ligand. This implies that the *endo*- and *exo*-H of the CH_2 cannot be distinguished. A similar observation has been reported for $[Mn(\eta^4\text{-cyclohexadiene})(CO)_3]^-$. In the ^{13}C–^1H-coupled NMR spectrum, the different coupling constants (121.3 and 136.6 Hz) of the two H atoms on the CH_2 peak (δ 46.03), did, however, finally distinguish between the *endo*- and *exo*-H.

Crystal data

$[K(C_{18}H_{36}N_2O_6)][Mn(C_5H_6)(CO)_3]$
M_r = 620.66
Triclinic, $P\overline{1}$
a = 11.5443 (5) Å
b = 11.7528 (5) Å
c = 12.5534 (6) Å
α = 110.307 (1)°
β = 109.523 (1)°
γ = 91.279 (1)°
V = 1486.98 (11) Å^3
Z = 2
D_x = 1.386 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6417 reflections
θ = 2.0–30.0°
μ = 0.64 mm^{-1}
T = 150 (2) K
Block, yellow
0.38 × 0.35 × 0.35 mm

Data collection

Bruker AXS SMART APEX diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.794, T_{max} = 0.808
19 143 measured reflections
9907 independent reflections
9068 reflections with $I > \sigma(I)$
R_{int} = 0.016
θ_{max} = 32.5°
$h = -17 \rightarrow 17$
$k = -17 \rightarrow 17$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.101
S = 1.26
9907 reflections
376 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

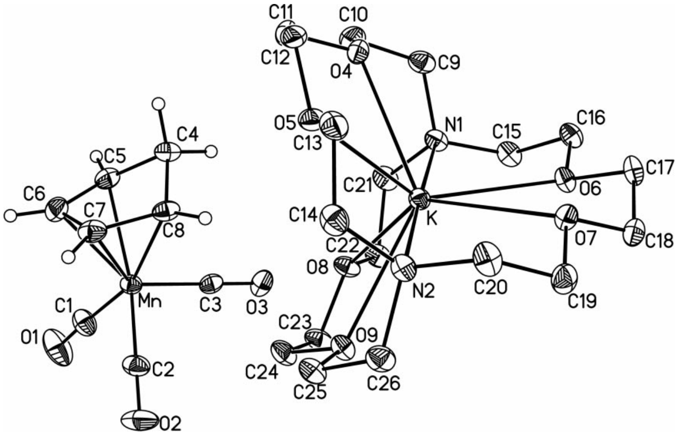


Figure 1
The molecular structure of the title compound. Ellipsoids are shown at the 50% probability level.

Table 1
Selected geometric parameters (Å).

Mn—C2	1.778 (1)	O2—C2	1.166 (2)
Mn—C3	1.780 (1)	O3—C3	1.161 (1)
Mn—C1	1.785 (1)	C4—C8	1.516 (2)
Mn—C7	2.083 (1)	C4—C5	1.516 (2)
Mn—C6	2.088 (1)	C5—C6	1.424 (2)
Mn—C5	2.149 (1)	C6—C7	1.417 (2)
Mn—C8	2.149 (1)	C7—C8	1.424 (2)
C1—O1	1.161 (2)		

Idealized atomic positions were calculated for the cryptate H atoms [d(C—H) = 0.96 Å, $U_{iso} = 1.2U_{eq}$ of the attached atom]. The remaining H atoms were located from a difference Fourier map and refined isotropically.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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