Synthesis of Dihydrooctamethyl-*s*-indacene: Synthesis and Structures of Organometallic Derivatives

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*Summary: Multi-gram quantities of 1,5-dihydro-1,2,3,4,5,6,7,8-octamethyl-s-indacene (Ic*H$_2$)* **(4)** *may be obtained via a four-step synthesis from p-xylene. Reaction with Cr(CO)$_3$(NH$_3$)$_3$ or $\{Cp^*Rh(acetone)_3\}^{2+}(SbF_6^-)_2$ yields (η^6-Ic*H$_2$)Cr(CO)$_3$* **(5)** *or $\{(\eta^5$-Ic*H)RhCp*$\}^+SbF_6^-$* **(6)***, respectively, while reaction of K$^+$(Ic*H)$^-$* **(7)** *and Mn(CO)$_3$(py)$_2$Br gives the exo and endo isomers of (η^5-Ic*H)Mn(CO)$_3$* **(8a,b)***. Single-crystal X-ray structures of* **6** *and* **8a** *have been determined.*

Oligomers or polymers based on metallocenes bridged by fused-ring ligands such as pentalene or *s*-indacene are anticipated to show interesting delocalized properties.[1] Indeed, ESR, Mössbauer, electrochemical, and magnetic data show very strong metal−metal interactions in the bimetallic species $\{L(MCp^*)_2\}^{n+}$ {L = pentalene, *s*-indacene; M = Fe, Co, Ni; *n* = 0, 1 2}.[2] However, the stepwise construction of higher oligomers has been hampered by escalating insolubility with increasing oligomerization.[3] We, therefore, perceived a requirement for a cost effective large scale synthesis of a fused-ring ligand bearing solubilizing substituents. In this communication we report the synthesis of 1,5-dihydro-1,2,3,4,5,6,7,8-octamethyl-*s*-indacene (Ic*H$_2$) (**4**) and some investigations of its organometallic chemistry.

Scheme 1 shows the route used for the synthesis of **4** which is based on previously published preparations of 1,2,3,4,5,6,7-heptamethylindene.[4−6] 2,3,4,7-Tetramethylindan-1-one was formed as an approximately 3:1 mixture of the isomers **1a,b**. The isomers of the ketone precursor to Ic*H$_2$, **3a**,**b**, were present in an approximate ratio of 2:1; they could be separated by fractional crystallization, and their structural formulas were confirmed by ^{1}H:^{1}H NOESY experiments. The solubility of **4** is surprisingly poor (*ca.* 40 g L^{-1} in boiling toluene).

We have begun to investigate the organometallic chemistry of **4** (Scheme 2). The conditions for the preparation of (η^6-Ic*H$_2$)Cr(CO)$_3$ (**5**) were chosen in analogy to those used in the synthesis of (η^6-heptamethylindene)Cr(CO)$_3$.[7] **5** has been characterized by mass spectrometry, ^{1}H and ^{13}C NMR, and IR spectroscopy.[21] ^{1}H and ^{13}C NMR spectra are consistent with an approximate 1:1:2 mixture of *endo*/*endo*, *exo*/*exo*, and *endo*/*exo* isomers. The IR spectrum of **5** (isomeric mixture, THF) shows two strong bands at 1863 and 1941 cm^{-1}; these are low frequencies for a (η^6-arene)-Cr(CO)$_3$ complex (for example, values of 1898, 1975 and 1862, 1943 cm^{-1} are reported for (η^6-indene)Cr(CO)$_3$[8] and one of the isomers of (η^6-heptamethylindene)Cr-(CO)$_3$,[7] respectively), reflecting the great electron richness of the Ic*H$_2$ ligand.

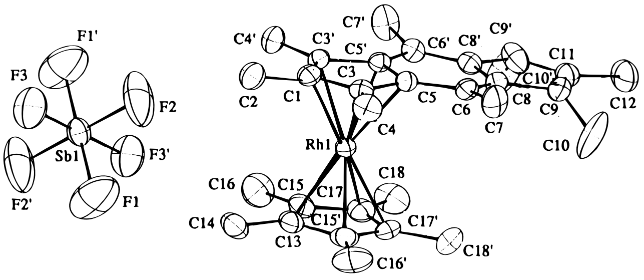

Figure 1. Molecular structure of **6**. Selected interatomic distances (Å): Rh(1)−C(1) 2.174(5), Rh(1)−C(3) 2.181(4), Rh(1)−C(5) 2.217(4), Rh(1)−C(13) 2.161(6), Rh(1)−C(15) 2.180(4), Rh(1)−C(17) 2.182(4). Primed atoms are generated by symmetry.

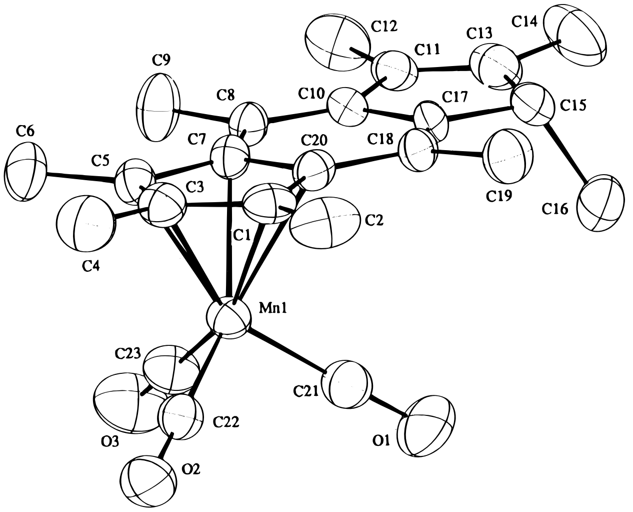

Figure 2. Molecular structure of **8a**. Selected interatomic distances (Å): Mn(1)−C(1) 2.125(5), Mn(1)−C(3) 2.137(5), Mn(1)−C(5) 2.128(5), Mn(1)−C(7) 2.185(5), Mn(1)−C(20) 2.197(5), Mn(1)−C(21) 1.763(7), Mn(1)−C(22) 1.743(6), Mn(1)−C(23) 1.766(6), O(1)−C(21) 1.160(7), O(2)−C(22) 1.167(7), O(3)−C(23) 1.164(7).

It has previously been shown by Maitlis and coworkers that indenes react with "Cp*M^{2+}" (M = Rh, Ir) to give η^6-indene complexes, which may rearrange to give η^5-indenyl species.[9] Bickert and Hafner have

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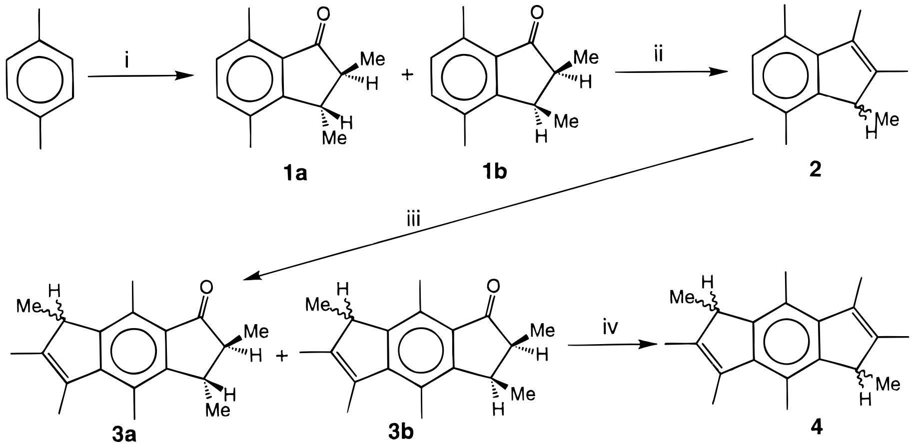
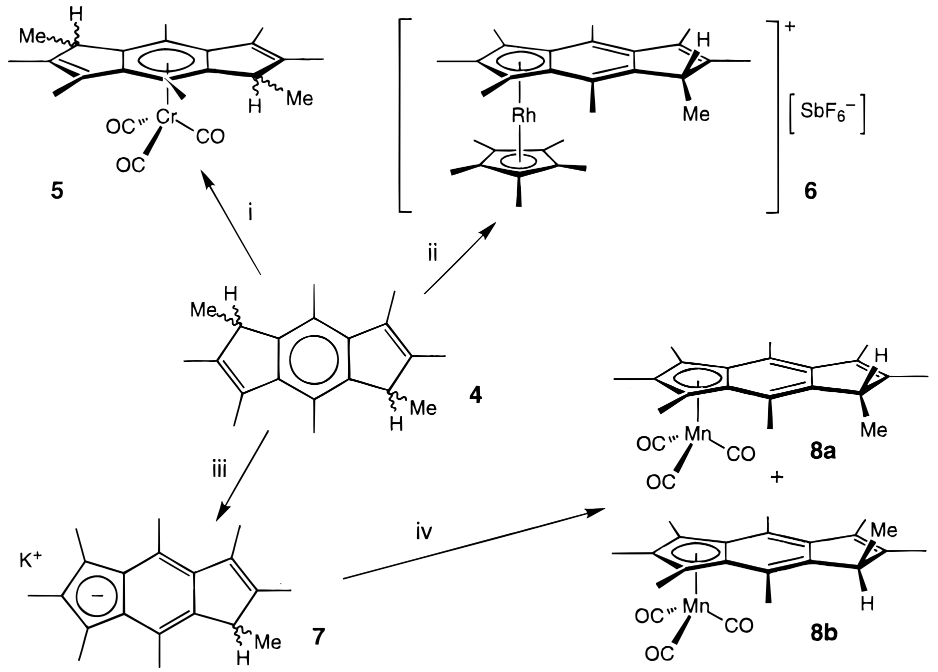
Scheme 1[a]



[a] Reagents and conditions: (i) $CH_3CH{=}C(CH_3)COCl$, $AlCl_3$, CH_2Cl_2, then concentrated HCl, 54%; (ii) CH_3MgI, petroleum ether (bp 40−60 °C), then concentrated HCl, yield 96%; (iii) $CH_3CH{=}C(CH_3)COCl$, $AlCl_3$, CH_2Cl_2, then concentrated HCl, yield 53%; (iv) CH_3MgI, petroleum ether (bp 40−60 °C), then concentrated HCl, yield 42%.

Scheme 2[a]



[a] Reagents and conditions: (i) $Cr(CO)_3(NH_3)_3$, refluxing 1,4-dioxane, yield 84%; (ii) $\{Cp^*Rh(acetone)_3\}^{2+}(SbF_6^-)_2$, acetone, yield 19%; (iii) K metal or KH, refluxing THF, quantitative; (iv) $Mn(CO)_3(py)_2Br$, THF, yield 49%.

extended the reaction to dihydro-*s*-indacenes.[10] We carried out the analogous reaction of $\{Cp^*Rh(acetone)_3\}^{2+}(SbF_6^-)_2$ and Ic^*H_2 by following the procedure of Bickert and Hafner;[10] an air-stable yellow material was crystallized by cooling the reaction mixture and was shown by NMR spectroscopy to be a single isomer of $\{(\eta^5\text{-}Ic^*H)RhCp^*\}^+SbF_6^-$ (**6**). The ^1H NMR shift of the Cp* methyl groups of **6** in acetone-d_6 (1.70 ppm) is somewhat upfield from the corresponding resonances in the same solvent for related species such as $\{(\eta^5\text{-}5\text{-}hydro\text{-}s\text{-}indacene)RhCp^*\}^+SbF_6^-$ (1.83 ppm),[10] reflecting the strong electron-donating power of the Ic*H ligand. Yellow single crystals of **6** were obtained by layering a dichloromethane solution with diethyl ether; a view of the molecular structure is shown in Figure 1.[22] The rhodium atom lies on a crystallographic mirror plane, which requires disorder between the "hydro" (5-position)

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and "non-hydro" (7-position) of the indacene ring. However, it is clear that the methyl group in the 5-position is on the same face of the ring system as the RhCp* fragment; i.e. the isomer isolated is {(5-*endo*-CH_3)(η^5-Ic*H)RhCp*}$^+$SbF_6^-. The pattern of long and short Rh−C Ic*H bonds is typical of η^5-indenyl type metal structures. The average Rh−C bond length is similar to those for [Rh{η^5-1,2,3-$C_5H_2(CO_2Me)_3$}$_2$]$^+${$C_5(CO_2Me)_5$}$^-$ [11] and {(η^5:η^5-fulvalene)(RhCp*)$_2$}$^{2+}$(PF_6^-)$_2$,[12] the only two rhodocenium salts to have been structurally characterized previously, and significantly shorter than those for Rh(C_5Ph_4H)$_2$.[13] The Cp* ring and the η^5-Ic*H ring completely eclipse one another, whereas in Rh{η^5-1,2,3-$C_5H_2(CO_2Me)_3$}$_2$$^+${$C_5(CO_2Me)_5$}$^-$ the two rings are staggered.

K$^+$(Ic*H)$^-$ (**7**) is much more soluble in solvents such as THF and benzene than **4**. Surprisingly, even when excess potassium or potassium hydride was used, no evidence was found for the formation of the dianion (Ic*)$^{2-}$. Investigations are currently taking place in our laboratory into the possibility of using more extreme conditions to doubly deprotonate **4**. (η^5-Ic*H)Mn(CO)$_3$ (**8**) is formed as a mixture of two isomers, **8a**,**b**, and is also much more soluble in common organic solvents than the parent hydrocarbon; the solubility of **8** in petroleum ether at 20 °C is approximately the same as that of **4** in boiling toluene. The infrared spectrum of **8** (isomeric mixture, CH_2Cl_2) shows two intense carbonyl stretching bands at 1914 and 2001 cm^{-1}. These are rather low frequencies for cyclopentadienyl-type Mn(CO)$_3$ complexes (e.g., for (η^5-5-hydro-*s*-indacene)Mn(CO)$_3$ values of 1930 and 2004 cm^{-1} are reported[14]), again reflecting the great electron-donating power of the permethylated indacene ligand system. Single crystals of the less soluble minor isomer, **8a**, were grown by cooling a pentane solution containing an isomeric mixture of **8a**,**b**.[22] A view of the molecular structure is shown in Figure 2; **8a** is revealed to be the *endo* isomer. The structure shows two relatively long and three short Mn−C ring distances, which is typical for indenyl metal structures. The M−C carbonyl bond lengths for **8a** are significantly shorter than those of other indacene Mn(CO)$_3$ complexes[14,15] (e.g. (η^5-5-hydro-*s*-indacene)Mn(CO)$_3$ has an average Mn−carbonyl bond length of 1.788(6) Å[14]). The C−O bond lengths are correspondingly longer in **8a** than in the other complexes (average for (5-hydro-*s*-indacene)Mn(CO)$_3$ 1.149 Å[14]).

Acknowledgment. We thank the EPSRC for support and for a studentship (S.B.).

Supporting Information Available: Text giving details of the synthetic procedures for compounds **1**−**8** and tables of crystal data and data collection details, fractional coordinates and *U* values, bond distances and angles, and anisotropic thermal parameters (8 pages). Ordering information is given on any current masthead page.

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[21] NMR data: (δ in ppm) are as follows. **4** ($CDCl_3$): δ_H 1.25 (d, 6H, J = 7.5 Hz, $\mathrm{CHC}H_3$), 1.95 (s, 6H, $\mathrm{C}H_3$), 2.23 (s, 6H, $\mathrm{C}H_3$), 2.56 (s, 6H, $\mathrm{C}H_3$), 3.18 (q, 2H, J = 7.5 Hz, $\mathrm{C}H$); δ_C 12.2 ($C\mathrm{H}_3$), 14.5 ($C\mathrm{H}_3$), 15.9 ($C\mathrm{H}_3$), 16.0 ($C\mathrm{H}_3$), 46.1 ($C\mathrm{H}$), 122.9 (quat), 132.1 (quat), 140.1 (quat), 142.6 (quat), 147.3 (quat). **5** (isomeric mixture) (C_6D_6): δ_H 0.89 (d, J = 7.5 Hz, *exo* $\mathrm{CHC}H_3$), 0.96 (d, J = 7.5 Hz, *exo* $\mathrm{CHC}H_3$), 1.26 (d, J = 7.5 Hz, *endo* $\mathrm{CHC}H_3$), 1.31 (d, J = 7.5 Hz, *endo* $\mathrm{CHC}H_3$), 1.51, (s, 2 × $\mathrm{C}H_3$), 1.58 (s, $\mathrm{C}H_3$), 1.59 (s, $C\mathrm{H}_3$), 1.87 (s, $C\mathrm{H}_3$), 1.90 (s, $C\mathrm{H}_3$), 1.92 (s, $C\mathrm{H}_3$), 2.00 (s, $C\mathrm{H}_3$), 2.22 (s, $C\mathrm{H}_3$), 2.23 (s, $C\mathrm{H}_3$), 2.27 (s, $C\mathrm{H}_3$), 2.39 (s, $C\mathrm{H}_3$), 2.60 (q, J = 7.5 Hz, $\mathrm{C}H$), 2.62 (q, J = 7.5 Hz, $\mathrm{C}H$), 2.93 (q, J = 7.5 Hz, $\mathrm{C}H$), 3.30 (q, *ca.* 1H, J = 7.5 Hz, $\mathrm{C}H$); δ_C 12.0 ($\mathrm{C}H_3$), 12.3 (2 × $\mathrm{C}H_3$), 12.4 ($\mathrm{C}H_3$), 13.8 (2 × $\mathrm{C}H_3$), 14.7 ($\mathrm{C}H_3$), 14.8 ($\mathrm{C}H_3$), 14.9 ($\mathrm{C}H_3$), 15.1 ($\mathrm{C}H_3$), 15.4 ($\mathrm{C}H_3$), 16.3 (2 × $\mathrm{C}H_3$), 16.4 ($\mathrm{C}H_3$), 19.7 ($\mathrm{C}H_3$), 20.2 ($\mathrm{C}H_3$), 45.5 ($C\mathrm{H}$), 45.8 ($C\mathrm{H}$), 45.9 ($C\mathrm{H}$), 46.6 ($C\mathrm{H}$), 93.3 (quat), 94.6 (quat), 104.2 (quat), 104.9 (quat), 108.6 (quat), 113.3 (quat), 115.0 (quat), 117.4 (quat), 117.7 (quat), 118.5 (quat), 120.8 (quat), 122.6 (quat), 130.2 (quat), 130.3 (quat), 130.4 (quat), 131.0 (quat), 144.1 (quat), 147.1 (quat), 147.2 (quat), 147.9 (quat), 236.7 ($C\mathrm{O}$). Anal. Calcd for $C_{23}H_{26}CrO_3$ (1:1:2 isomeric mixture): C, 68.64; H, 6.51. Found: C, 67.79; H, 6.03. MS (EI): m/z 402 (M^+). **6** (CD_2Cl_2): δ_H 1.24 (d, 3H, J_{HH} = 7.3 Hz, $\mathrm{CHC}H_3$), 1.57 (s, 15H, Cp* $\mathrm{C}H_3$), 1.82 (s, 3H, Ic*H $\mathrm{C}H_3$), 1.96 (s, 3H, Ic*H $\mathrm{C}H_3$), 2.21 (s, 3H, Ic*H $\mathrm{C}H_3$), 2.26 (s, 3H, Ic*H $\mathrm{C}H_3$), 2.27 (s, 3H, Ic*H $\mathrm{C}H_3$), 2.43 (s, 3H, Ic*H $\mathrm{C}H_3$), 2.60 (s, 3H, Ic*H $\mathrm{C}H_3$), 3.26 (q, 1H, J_{HH} = 7.3 Hz, $\mathrm{C}H$); δ_C 8.2 (s, Cp* $C\mathrm{H}_3$), 8.8 (s, Ic*H $C\mathrm{H}_3$), 12.0 (s, Ic*H $C\mathrm{H}_3$), 12.4 (s, Ic*H $C\mathrm{H}_3$), 12.9 (s, Ic*H $C\mathrm{H}_3$), 15.3 (s, Ic*H $C\mathrm{H}_3$), 16.1 (s, Ic*H $C\mathrm{H}_3$), 17.3 (s, Ic*H $C\mathrm{H}_3$), 17.6 (s, Ic*H $C\mathrm{H}_3$), 45.7 (s,$C\mathrm{H}$), 91.8 (d, J_{RhC} = 6.5 Hz, Ic*H RhC), 91.9 (d, J_{RhC} = 7.5 Ic*H RhC), 98.0 (d, J_{RhC} = 7.0 Hz Cp* RhC), 100.8 (d, J_{RhC} = *ca.* 5 Hz, Ic*H RhC), 102.9 (d, J_{RhC} = *ca.* 9 Hz, Ic*H RhC), 103.9 (d, J_{RhC} = *ca.* 6 Hz, Ic*H RhC), 117.9 (s, Ic*H quat), 122.1 (s, Ic*H quat), 132.3 (s, Ic*H quat), 146.2 (s, Ic*H quat), 149.8 (s, Ic*H quat). Anal. Calcd for $C_{30}H_{40}RhSbF_6$: C, 48.74; H, 5.45. Found: C, 48.74; H, 6.03. **7** (C_6D_6): δ_H 1.14 (d, 3H, J = 6.5 Hz, $\mathrm{CHC}H_3$), 1.88 (s, 3H, $\mathrm{C}H_3$), 1.92 (s, 3H, $\mathrm{C}H_3$), 2.20 (s, 3H, $\mathrm{C}H_3$), 2.25 (s, 3H, $\mathrm{C}H_3$), 2.30 (s, 3H, $\mathrm{C}H_3$), 2.39 (s, 3H, $\mathrm{C}H_3$), 2.67 (s, 3H, $\mathrm{C}H_3$), 3.08 (q, 1H, J = 6.4 Hz, $\mathrm{C}H$); δ_C 10.9 ($C\mathrm{H}_3$), 12.5 ($C\mathrm{H}_3$), 13.2 ($C\mathrm{H}_3$), 14.0 ($C\mathrm{H}_3$), 15.9 ($C\mathrm{H}_3$), 16.8 ($C\mathrm{H}_3$), 17.3 ($C\mathrm{H}_3$), 18.4 ($C\mathrm{H}_3$), 45.1 ($C\mathrm{H}$), 98.2 (quat), 99.1 (quat), 116.8 (quat), 118.7 (quat), 122.0 (quat), 123.9 (quat), 124.2 (quat), 131.2 (quat), 133.0 (quat), 134.1 (quat), 137.7 (quat). **8a** (C_6D_6): δ_H 1.02 (d, 3H, J = 7.0 Hz, $\mathrm{CHC}H_3$), 1.60 (s, 3H, $\mathrm{C}H_3$), 1.66 (s, 6H, $\mathrm{C}H_3$), 1.98 (s, 3H, $\mathrm{C}H_3$), 2.13 (s, 3H, $\mathrm{C}H_3$), 2.14 (s, 3H, $\mathrm{C}H_3$), 2.38 (s, 3H, $\mathrm{C}H_3$), 2.65 (s, 3H, $\mathrm{C}H_3$), 2.97 (q, 1H, J = 7.0 Hz, $\mathrm{C}H$); δ_C 10.5 ($C\mathrm{H}_3$), 12.3 ($C\mathrm{H}_3$), 13.3 ($C\mathrm{H}_3$), 13.7 ($C\mathrm{H}_3$), 15.2 ($C\mathrm{H}_3$), 16.2 ($C\mathrm{H}_3$),16.3 ($C\mathrm{H}_3$), 17.0 ($C\mathrm{H}_3$), 45.3 ($C\mathrm{H}$), 85.3 (quat), 87.5 (quat), 101.7 (quat), 104.1 (quat), 122.0 (quat), 123.5 (quat), 132.4 (quat), 142.0 (quat), 145.2 (quat), 145.8 (quat), 227.3 ($C\mathrm{O}$) (remaining quat obscured by solvent). **8b** (C_6D_6): δ_H 1.04 (d, 3H, J = 7.0 Hz, $\mathrm{CHC}H_3$), 1.60 (s, 3H, $\mathrm{C}H_3$), 1.63 (s, 6H, $\mathrm{C}H_3$), 1.98 (s, 3H, $\mathrm{C}H_3$), 2.07 (s, 3H, $\mathrm{C}H_3$), 2.14 (s, 3H, $\mathrm{C}H_3$), 2.32 (s, 3H, $\mathrm{C}H_3$), 2.65 (s, 3H, $\mathrm{C}H_3$), 2.78 (q, 1H, J = 7.0 Hz, $\mathrm{C}H$); δ_C 10.6 ($C\mathrm{H}_3$),12.2 ($C\mathrm{H}_3$), 12.5 ($C\mathrm{H}_3$), 12.8 ($C\mathrm{H}_3$), 13.6 ($C\mathrm{H}_3$), 15.2 ($C\mathrm{H}_3$), 16.2 ($C\mathrm{H}_3$), 16.9 ($C\mathrm{H}_3$), 44.9 ($C\mathrm{H}$), 86.3 (quat), 86.6 (quat), 100.2 (quat), 103.8 (quat), 122.1 (quat), 123.5 (quat), 132.4 (quat), 142.5 (quat), 145.5 (quat), 145.6 (quat), 227.3 ($C\mathrm{O}$) (remaining quat obscured by solvent). Anal. Calcd for $C_{23}H_{25}MnO_3$ (1:1 isomeric mixture): C, 68.31; H, 6.23. Found: C, 68.97; H, 6.37. MS (EI): m/z 404 (M^+).

[22] Crystal data are as follows. **6**: $C_{30}H_{40}RhSbF_6$, M_r = 739.30, monoclinic, $P2_1/m$, a = 8.9611(9) Å, b = 17.535(2) Å, c = 9.5300(8) Å, b = 100.611(8), V = 1471.9(3) Å^3, Z = 2, D_c = 1.66 g cm^{-3}, μ = 15.3 cm^{-1}, $F(000)$ = 740, crystal size *ca.* 0.09 × 0.36 × 1.05 mm, 4898 total (3965 independent) reflections, R = 0.042 and R_w = 0.049 for 2752 reflections with $I > 3\sigma(I)$. **8a**: $C_{23}H_{25}MnO_3$, M_r = 404.40, orthorhombic, *Pbca*, a = 13.824(4) Å, b = 15.920(4) Å, c = 18.493(4) Å, V = 4070(1) Å^3, Z = 8, D_c = 1.32 g cm^{-3}, μ = 6.41 cm^{-1}, $F(000)$ = 1696, crystal size *ca.* 0.54 × 0.60 × 0.81 mm, 4958 total (3559 independent) reflections, R = 0.053 and R_w = 0.058 for 1752 reflections with $I > 3\sigma(I)$. Room-temperature data for both crystals were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation, employing $\omega-2\theta$ scans (θ_{max} = 29° for **6**, θ_{max} = 25° for **8a**). Corrections were made for Lorentz and polarization effects.[16] Both structures were solved by direct methods using SIR92[17] and refined using full-matrix least squares. Absorption corrections were applied using DIFABS.[18] Chebyshev weighting schemes[19] were applied in the refinements and corrections for the effects of anomalous dispersion and isotropic extinction (*via* an overall extinction parameter).[20] In the structure of **6** a crystallographic mirror plane bisects the cation; this requires disorder between the in-plane 7-methyl group and the out-of-plane 5-methyl. Attempts to model the disorder with two atoms were unsuccessful so C(10) was refined as a composite of the two sites.