Convenient Solution Route To Alkylated Pentalene Ligands: New Metal Monoalkylpentalenyl Complexes

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Carbene-induced rearrangement of 8,8-dibromobicyclo[5.1.0]octa-2,4-dienes and subsequent in situ deprotonation of the dihydropentalenes formed represents a straightforward and versatile solution route to pentalene ligands for use in organometallic chemistry. We report here the synthesis of 6-alkyl-substituted 8,8-dibromobicyclo[5.1.0]octa-2,4-dienes and their rearrangement to give correspondingly substituted pentalene ligands. Generation of methyl-substituted dihydropentalenes from 8,8-dibromo-6-methylbicyclo-[5.1.0]octa-2,4-diene followed by monodeprotonation with TlOEt gives methylhydropentalenyl salts, Tl-(C_8H_6Me), as a mixture of isomers. Formation of both 1-Me and 3-Me isomers of $Re(C_8H_6Me)(CO)_3$ from these Tl species shows that monodeprotonation of the dihydropentalenes occurs at the unsubstituted ring. No evidence for the 2-Me isomer is observed, consistent with the rearrangement mechanism reported in the literature. Likewise, rearrangement of 8,8-dibromo-6-alkylbicyclo[5.1.0]octa-2,4-dienes (R = Me, Et, ^{i}Pr) and subsequent double deprotonation with ^{n}BuLi in the presence of DME affords the pentalenyl salts $Li_2(C_8H_5R)\cdot x$DME. X-ray crystallographic studies of the dinuclear Mn organometallics *anti*-[Mn-$(CO)_3]_2(C_8H_5R)$ synthesized from the Li salts confirm that these alkylated pentalene ligands are substituted at the 1-position exclusively. The crystal structure of a model hydropentalenyl complex, $Re(C_8H_7)(CO)_3$, is also reported.

Introduction

Organometallic polymers with metals in the polymer chain are of significant current interest due to their application as advanced electronic, optical, and magnetic materials;[1] in particular, polymers that feature metal units connected by way of conjugated organic spacers have potential utility as "molecular wires".[2,3] Through-bond metal−metal electronic interaction in multinuclear metallocene-like species can be significant when the metal units are connected via a common π-system such as a conjugated, fused-ring polycyclic hydrocarbon ligand (Figure 1a): for example, naphthalene, indene, or *s*-indacene.[4,5] Such species may be considered as model systems for conjugated metallocene polymers or as the building blocks of the polymers themselves.[6] Recently, pentalene (which may be regarded as the bicyclic homologue of cyclopentadiene) has been demonstrated as a superlative ligand for the facilitation of metal−metal interaction in a series of anti-bimetallic complexes; the extent of electronic delocalization in the mixed-valence forms of these dinuclear species has been probed by a variety of experimental techniques and shown to be among the largest reported for hydrocarbon-bridged organometallics.[7,8] Unfortunately, attempts to extend these investigations to oligomeric materials have been hampered by the solubility of higher nuclearity species. Manriquez et al. have outlined an iterative synthetic route to metal−pentalene oligomers via the deprotonation of a hydropentalenyl complex and subsequent reaction with an "MX_n" synthon; however, they report the trinuclear complex (η^5-PnH)Fe(μ,η^5:η^5-Pn)Fe(μ,η^5:η^5-Pn)Fe(η^5-PnH) (Figure 1b) (PnH = hydropentalenyl, C_8H_7; Pn = pentalenyl, C_8H_6) to be very insoluble in common solvents (ca. 400 mg L^{-1} in boiling toluene), precluding characterization by solution methods and preventing extension of this synthesis to species with four or more nuclei.[9] One possible way to increase the processibility of oligomers of this type is to use a pentalene ligand substituted with a suitable solubilizing group (e.g. alkyl, alkoxy). Hence, a straightforward route to substituted pentalene ligands is desirable.

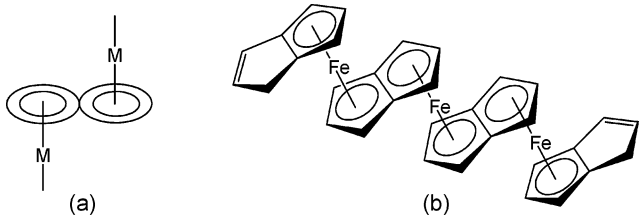

Figure 1. (a) Schematic of metal units connected via a fused-ring polycyclic hydrocarbon ligand. (b) Trinuclear (η^5-PnH)Fe(μ,η^5:η^5-Pn)Fe(μ,η^5:η^5-Pn)Fe(η^5-PnH) reported by Manriquez et al.

(1) For recent reviews, see: (a) Nguyen, P.; Gomez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515−1548. (b) Holliday, B. J.; Swager, T. M. *Chem. Comm.* **2005**, 23−36. (c) Pittman, C. U. *J. Inorg. Organomet. Polym. Mater*. **2005**, *15*, 33−55.

(2) (a) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 179−444. (b) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178*−*180*, 431−509.

(3) Ward, M. D. *Chem. Soc. Rev.* **1995**, 121−134.

(4) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637−669.

(5) Ceccon, A.; Santi, S.; Orian, L.; Bisello, A. *Coord. Chem. Rev.* **2004**, *248*, 683−724.

(6) Calculations suggest that extended polymetallic sandwich compounds should be stable for certain metal/ligand combinations. See: Burdett, J. K.; Canadell, E. *Organometallics* **1985**, *4*, 805−815.

(7) Manriquez, J. M.; Ward, M. D.; Reiff, W. M.; Calabrese, J. C.; Jones, N. L.; Carroll, P. J.; Bunel, E. E.; Miller, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 6182−6193.

(8) Jones, S. C.; Hascall, T.; Barlow, S.; O'Hare, D. *J. Am. Chem. Soc.* **2002**, *124*, 11610−11611.

(9) Oelckers, B.; Chávez, I.; Manriquez, J. M.; Román, E. *Organometallics* **1993**, *12*, 3396−3397.

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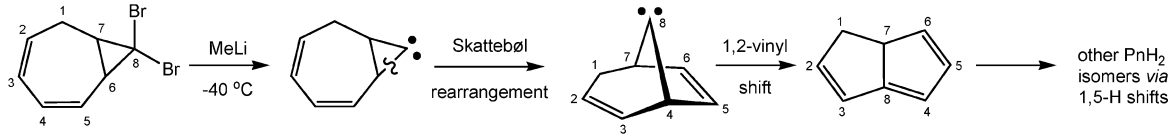
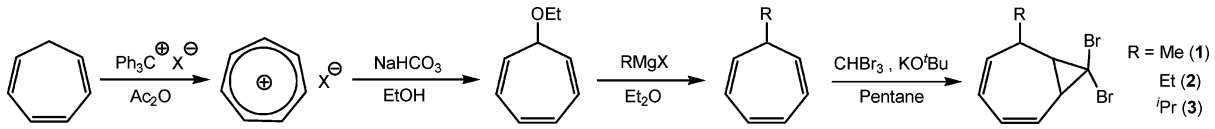


Figure 2. Mechanism of the rearrangement of 8,8-dibromobicyclo[5.1.0]octa-2,4-diene to dihydropentalenes, after ref 20. The numbering scheme reflects the nomenclature for substituted pentalene ligands used in this work and is not the standard IUPAC format for bicyclic ring systems.

Scheme 1



The majority of pentalene organometallics have their ligand source in the hydropentalenyl anion, $[PnH]^-$, or the pentalenyl dianion, $[Pn]^{2-}$, which may be formed respectively by single and double deprotonation of dihydropentalene, PnH_2. Syntheses of substituted pentalene ligands remain scarce, in part due to difficulties involved in the formation of PnH_2 and its derivatives.[10] Synthetic routes to dihydropentalenes include Katz's original preparation of PnH_2 via flash vacuum pyrolysis (FVP) of isocyclopentadiene[11] and the thermal rearrangement of 6-vinylfulvenes.[12−14] Cloke et al. have recently reported the formation of silylated pentalene ligands by reaction of $[Pn]^{2-}$ with triakylsilyl electrophiles;[15] these 1,4-bis(trialkylsilyl)-pentalene ligands[16] have found utility in the chemistry of both mono- and dinuclear pentalene complexes of the transition metals and f elements.[17] Cloke's synthesis of PnH_2 employs FVP of cyclooctatetraene in the gas phase at high temperature (400−675 °C);[18] this has been carefully optimized to give PnH_2 in high yield using specialized apparatus. A simple, nonpyrolytic route to PnH_2 by treatment of 8,8-dibromobicyclo[5.1.0]octa-2,4-diene with MeLi at low temperature has been reported by Baird and Reese.[19] The mechanism of this reaction has been determined by Fleischhauer and Brinker via ^{12}C-labeling studies,[20] shown to be analogous to the Skattebøl rearragement of vinyl-*gem*-dibromocyclopropanes to cyclopentadienes;[21] this proceeds through the generation of a carbene intermediate which undergoes bond cleavage and a series of rearrangements to form PnH_2, as outlined in Figure 2. This reaction has been exploited as a route to the pentalenyl dianion, although with limited success (ca. 30% yield);[22] however, recent optimization in this laboratory has afforded Li_2Pn as its DME adduct in up to 90% isolated yield (see the Experimental Section). 8,8-Dibromobicyclo-[5.1.0]octa-2,4-diene is a readily available starting material (formed by addition of dibromocarbene to cycloheptatriene (CHT)), and its carbene-induced rearragement to give PnH_2 has advantage over FVP syntheses, as the reaction can be performed in solution using standard laboratory techniques. Accordingly, we were interested to determine whether rearrangement of substituted 8,8-dibromobicyclo[5.1.0]octa-2,4-dienes could be used to prepare the corresponding substituted pentalene ligands. We report here a rational synthesis of monoalkylated pentalene ligands utilizing a straightforward solution route based on the ring expansion of 7-alkylcycloheptatrienes and the characterization of these ligands through formation of a series of organometallic complexes.

Results and Discussion

Synthesis of Alkyl-Substituted Dihydropentalenes. 7-Alkylcycloheptatrienes were prepared via a general synthesis from CHT. Initial hydride abstraction gave the 6-π-aromatic tropylium ion, which was subsequently converted into an ether and the alkoxy group then substituted using the appropriate Grignard reagent; the Grignard reagent can be reacted directly with the tropylium intermediate, but yields are poorer due to the low solubility of common salts of the tropylium cation. 7-Alkylcycloheptatrienes (R = Me, Et, ^{i}Pr, ^{t}Bu) were formed accordingly in high yields (75−90%). Reaction of these with $CHBr_3$ and KO^{t}Bu in pentanes (Scheme 1) afforded 8,8-dibromo-6-alkylbicyclo[5.1.0]octa-2,4-dienes when R = Me (**1**), Et (**2**), ^{i}Pr (**3**), although the reaction failed when R = ^{t}Bu (possibly the steric bulk of the ^{t}Bu group hinders attack by dibromocarbene).[23] The product 8,8-dibromo-6-alkylbicyclo[5.1.0]octa-2,4-dienes were fully characterized. C6 is chiral, and consequently the CH_2 protons of **2** and Me groups of **3** appear diastereotopic in their respective ^1H (**2**, **3**) and ^{13}C (**3**) NMR spectra; this diastereotopy is also a feature of the respective dilithium and dimanganese species **10**, **11**, **13**, and **14** discussed below. **1**−**3** were reacted with MeLi at −45 °C to form dihydropentalenes as outlined above; these dihydropentalenes were not themselves isolated[24] but reacted in situ to form hydropentalenyl or pentalenyl complexes, as described in the following sections.

Hydropentalenyl Complexes. Dihydropentalenes can be deprotonated once at the cyclopentadiene-like ring to give salts

(10) For a comprehensive review of pentalene and dihydropentalene syntheses, see: Lindner, H.-J. In *Methoden der Organischen Chemie*, 4th ed.; Georg Thieme Verlag: Stuttgart, Germany, 1985; Vol. 5/2c, pp 103−122.

(11) (a) Katz, T. J.; Rosenberger, M. *J. Am. Chem. Soc.* **1962**, *84*, 865−866. (b) Katz, T. J.; Rosenberger, M.; O'Hara, R. K. *J. Am. Chem. Soc.* **1964**, *86*, 249−252.

(12) Gajewski, J. J.; Cavender, C. J. *Tetrahedron Lett.* **1971**, *12*, 1057−1060.

(13) Griesbeck, A. G. *Synthesis* **1990**, 144−147.

(14) (a) Kaiser, R.; Hafner, K. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 892−893. (b) Kaiser, R.; Hafner, K. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 335−337.

(15) Cloke, F. G. N.; Kuchta, M. C.; Harker, R. M.; Hitchcock, P. B.; Parry, J. S. *Organometallics* **2000**, *19*, 5795−5798.

(16) See Figure 2 for the numbering system used here for substituted pentalenes and dihydropentalenes. A pentalenyl ring (C_8H_{6-m}, where *m* is the number of substituents) substituted by R in the *n*-position is abbreviated Pn^{n-R} in the text; hence, 1-methyldihydropentalene is written $Pn^{1-Me}H_2$. Hydropentalenyl complexes are numbered so as to assign the uncoordinated ring lower substituent locants.

(17) Cloke, F. G. N. *Pure Appl. Chem.* **2001**, *73*, 233−238.

(18) Jones, M.; Schwab, L. O. *J. Am. Chem. Soc.* **1968**, *92*, 6549−6550.

(19) Baird, M. S.; Reese, C. B. *Tetrahedron Lett.* **1976**, *33*, 2895−2898.

(20) Fleischhauer, H.; Brinker, U. H. *Chem. Ber.* **1987**, *120*, 501−506.

(21) Skattebøl, L. *Chem. Ind.* **1962**, 2146−2147.

(22) Burger, U.; Bianco, B. *Helv. Chim. Acta* **1983**, *66*, 60−67.

(23) Addition of dichlorocarbene and dibromocarbene to CHT occurs regioselectively at the C1−C2 double bond. See: Kostikov, R. R.; Molchanov, A. P. *Zh. Org. Khim.* **1984**, *20*, 1003−1007.

(24) Simple dihydropentalenes are known to oligomerize readily upon standing at room temperature, although some are stable at low temperature under an inert atmosphere.[10,11,15]

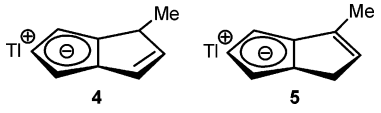


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Figure 3. Isomers $TlPn^{1-Me}H$ and $TlPn^{3-Me}H$.

of the $[PnH]^-$ anion. We identified TlOEt as a suitable base to ensure exclusive in situ monodeprotonation of dihydropentalenes formed by the rearrangement outlined above; these dihydropentalenes are not isolated, so use of ethoxide base avoids generation of $[Pn]^{2-}$ side product that could arise from a potential excess a of stronger base such as ^{n}BuLi.[25] TlPnH has previously been employed successfully as a source of $[PnH]^-$ for the formation of organometallic complexes; its preparation from dihydropentalene using aqueous alkali in the presence of Tl_2SO_4 was reported by Katz.[26,27] We synthesized TlPnH from the rearrangement of 8,8-dibromobicyclo[5.1.0]octa-2,4-diene at −45 °C followed by extraction of the dihydropentalenes generated and their subsequent deprotonation with TlOEt; this gave a light-sensitive yellow solid whose properties were identical with those described for TlPnH in the literature.[26,28] Likewise, a similar reaction of 8,8-dibromo-6-methylbicyclo-[5.1.0]octa-2,4-diene gave a light-sensitive yellow solid after workup, which was identified as $TlPn^{Me}H$ by high-resolution mass spectrometry; evidently rearrangement of the methyl-substituted 8,8-dibromobicyclo[5.1.0]octa-2,4-diene to dihydropentalenes occurs as desired here. ^{1}H and ^{13}C NMR spectroscopy showed this yellow solid to be a mixture of two isomers, tentatively assigned as $TlPn^{1-Me}H$ (**4**) and $TlPn^{3-Me}H$ (**5**) (Figure 3); the isomer ratio was determined to be ca. 3:1 by integration of the ^{1}H NMR resonances (the isomer with the least substituted double bond was found to be more abundant). Interpretation of the ^{1}H NMR spectra of **4** and **5** was hampered both by the similarity in chemical shift between the proton resonances of the Cp-like and olefinic rings and by the broad appearance of these resonances, which did not allow for successful extraction of structural data from the coupling patterns; we were therefore unable to determine unambiguously at which ring deprotonation had occurred in **4** and **5**. Hence, it was decided to form organometallic derivatives in an attempt to achieve clear distinction of proton resonances from the coordinated and uncoordinated rings and, thus, full identification of the $Pn^{Me}H$ isomers present.

A simple unsubstituted hydropentalenyl species was desired in order to serve as a model for organometallic complexes of the methylhydropentalenyl ligands. We chose to react TlPnH with 0.5 equiv of $[Re(CO)_3(THF)Br]_2$, which afforded $Re(\eta^5\text{-}PnH)(CO)_3$ (**6**) as a colorless crystalline solid.[29] The ^{1}H and ^{13}C NMR spectra of **6** were fully assigned, aiding subsequent identification of its methylated analogues as detailed below. An important spectral signature is seen for the H_1 protons, which

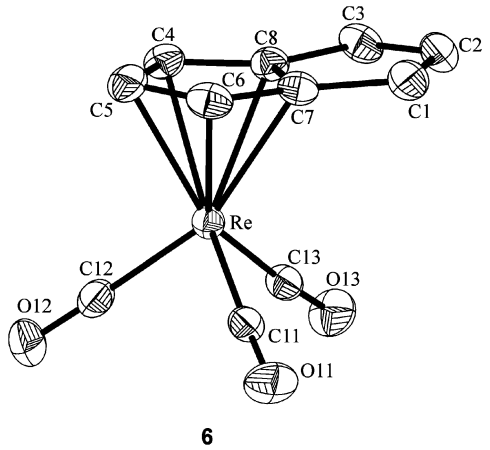

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Figure 4. Crystal structure of $Re(\eta^5\text{-}PnH)(CO)_3$ with thermal ellipsoids at the 50% probability level and all H atoms omitted for clarity.

are inequivalent due to their endo and exo orientation with regard to the $Re(CO)_3$ unit; these resonances appear in the ^{1}H NMR spectrum of **6** (500 MHz) as an AB quartet with strong two-bond coupling (J = 22 Hz).[30]

X-ray-quality single crystals were grown from Et_2O solution; the structure of **6** is shown in Figure 4, and important bond lengths are given in Table 1.[31] The ligand is not planar, with a hinge angle of 5.6° (defined as the angle between the least-squares planes containing atoms C1, C2, C3, C7, C8 and C4, C5, C6, C7, C8, respectively) directing the uncoordinated ring away from the metal center. Inspection of the C−C bond lengths and angles shows a clear distinction between the coordinated and uncoordinated rings; the mean C−C bond length in the coordinated ring (1.426 Å) is typical for Cp complexes,[32] while the significant difference between C1−C2 and C1−C3 bond lengths reveals the position of the C═C double bond between C2 and C3, and the respective bond angles in the uncoordinated ring are concomitantly deformed from the pentagonal ideal of 108°. The $Re-C_{ring}$, $Re-C_O$, and C−O distances are standard for η^5-carbocyclic $Re(CO)_3$ species: e.g., $Re(\eta^5\text{-}Cp)(CO)_3$.[33]

Similar reaction of a mixture of **4** and **5** with 0.5 equiv of $[Re(CO)_3(THF)Br]_2$ gave a mixture of $Re(\eta^5\text{-}Pn^{Me}H)(CO)_3$ isomers as a thick yellow oil; as for **4** and **5**, NMR spectroscopy revealed the existence of two isomers, although here the isomer ratio was determined to be ca. 1:1 from the ^{1}H spectrum. It did not prove possible to isolate one isomer from the other, either

(25) Organometallic hydropentalenyl complexes may themselves be deprotonated by strong base at the uncoordinated ring(s). See: (a) Katz, T. J.; Rosenberger, M. *J. Am. Chem. Soc.* **1963**, *85*, 2030−2031. (b) Burgos, F.; Chavez, I.; Manriquez, J. M.; Valderrama, M.; Lago, E.; Molins, E.; Delpech, F.; Castel, A.; Riviere, P. *Organometallics* **2001**, *20*, 1287−1291. (c) References 7, 9, and 26.

(26) Katz, T. J.; Mrowca, J. J. *J. Am. Chem. Soc*. **1967**, *89*, 1105−1111.

(27) Janiak, C. *Coord. Chem. Rev.* **1997**, *163*, 107−216.

(28) Fritz, H. P.; Köhler, F. *J. Organomet. Chem.* **1971**, *30*, 177−185.

(29) $Mn(\eta^5\text{-}PnH)(CO)_3$ has been obtained as a yellow oil from the cyclotetramerization of acetylene using $Mn_2(CO)_{10}$ or $MnMe(CO)_5$ (Coffield, T. H.; Ihrman, K. G.; Burns, W. *J. Am. Chem. Soc.* **1960**, *82*, 4209−4210); the authors' synthesis from TlPnH and $Mn(CO)_3(py)_2Br$ also afforded a yellow oil. It was therefore decided to attempt synthesis of the Re analogue in the hope that it would be a solid and, thus, its methylated analogues potentially be separable by fractional crystallization.

(30) Similar AB patterns are observed for these protons in the ^{1}H NMR spectra of other hydropentalenyl complexes, for example. (a) $Ru(\eta^5\text{-}PnH)(Mn(CO)_5)(CO)_2$: Knox, S. A. R.; McKinney, R. J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 235−239. (b) $Ru(\eta^5\text{-}PnH)(\eta^5\text{-}Cp^*)$: Burgos, F.; Arancibia, V.; Manriquez, J. M.; Chavez, I. *Bol. Soc. Chil. Quim.* **2000**, *45*, 621−628. (c) $Mn(\eta^5\text{-}PnH)(CO)_3$: Jones, S. C.; O'Hare, D. Unpublished results.

(31) For other organometallic hydropentalenyl complexes that have been characterized crystallographically, see: (a) Molins, E.; Maniukiewicz, W.; Miravitlles, C.; Mas, M.; Manriquez, J. M.; Chavez, I.; Oelckers, B.; Farran, J.; Brianso, J. L. *Acta Crystallogr*. **1996**, *C52*, 2414−2416. (b) Alvarez-Larena, A.; Brianso, J. L.; Piniella, J. F.; Farran, J.; Manriquez, J. M.; Chavez, I.; Oelckers, B.; Molins, E.; Miravitlles, C. *Acta Crystallogr*. **1996**, *C52*, 2754−2757. (c) Miravitlles, C.; Molins, E.; Maniukiewicz, W.; Mas, M.; Manriquez, J. M.; Chavez, I.; Oelckers, B.; Alvarez-Carena, A.; Brianso, J. L. *Acta Crystallogr*. **1996**, *C52*, 3047−3049. (d) Komatsu, H.; Suzuki, Y.; Yamazaki, H. *Chem. Lett.* **2001**, 998−999. Structures of two substituted dihydropentalenes have also been determined by X-ray crystallography; see: Bailey, P. M.; Mann, B. E.; Brown, I. D.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1976**, 238−239.

(32) Wheatley, P. J. In *Perspectives in Structural Chemistry*; Dunitz, J. D., Ibers, J. A., Eds.; Wiley: New York, 1967; Vol. 1, pp 1−40.

(33) Fitzpatrick, P. J.; Page, Y. L.; Butler, I. S. *Acta Crystallogr*. **1981**, *B37*, 1052−1058.

Table 1. Important Bond Lengths and Angles (with Esd's in Parentheses) for 6 and 12−14 alongside Comparative Data for *anti*-[Mn(CO)$_3$]$_2$(μ,η^5:η^5-Pn) (L1)[8]

param[a]	6	L1[b]	12	13	14
M1−C$_{ring}$ (mean)	2.310	2.166	2.161	2.164	2.166
M2−C$_{ring}$ (mean)			2.167	2.162	2.163
M1−C$_O$ (mean)	1.909	1.802	1.795	1.797	1.799
M2−C$_O$ (mean)			1.797	1.801	1.797
C−O$_{M1}$ (mean)	1.154	1.147	1.151	1.148	1.150
C−O$_{M2}$ (mean)			1.145	1.146	1.148
C1−C2	1.442(9)	1.425(2)	1.426(5)	1.429(2)	1.426(3)
C2−C3	1.377(9)	1.421(2)	1.419(5)	1.419(2)	1.412(3)
C3−C8	1.475(7)	1.445(2) [C3−C7′]	1.439(5)	1.449(2)	1.443(3)
C7−C8	1.424(7)	1.466(3) [C7−C7′]	1.460(5)	1.459(2)	1.467(3)
C1−C7	1.491(8)	1.443(2)	1.452(5)	1.451(2)	1.456(3)
C4−C8	1.424(7)		1.450(5)	1.449(2)	1.443(3)
C4−C5	1.435(8)		1.424(6)	1.417(2)	1.419(3)
C5−C6	1.423(8)		1.426(5)	1.425(2)	1.419(3)
C6−C7	1.425(7)		1.444(5)	1.444(2)	1.450(3)
C1−C20			1.471(5)	1.498(2)	1.510(3)
C20−C21				1.519(2)	1.519(3)
C20−C22					1.519(3)
C2−C1−C7	103.6(5)	106.6(1)	105.8(3)	105.4(1)	105.4(2)
C1−C2−C3	113.4(5)	110.9(1)	111.3(3)	111.6(1)	112.0(2)
C2−C3−C8	106.3(5)	106.8(1) [C2−C3−C7′]	106.8(3)	106.7(1)	106.7(2)
C5−C4−C8	106.4(5)		106.5(3)	106.8(1)	106.8(2)
C4−C5−C6	109.1(5)		111.1(3)	110.9(1)	110.8(2)
C5−C6−C7	107.4(5)		106.2(3)	106.5(1)	107.2(2)
C1−C7−C8	108.5(5)	107.8(2) [C1−C7−C7′]	108.1(3)	108.8(1)	108.1(2)
C6−C7−C8	108.0(5)		108.4(3)	108.0(1)	107.0(2)
C3−C8−C7	108.1(5)	107.6(2) [C3−C7′−C7]	107.7(3)	107.3(1)	107.5(2)
C4−C8−C7	109.0(4)		107.5(3)	107.5(1)	108.0(2)

[a] All bond lengths are in Å, and all bond angles are in deg. [b] **L1** is centrosymmetric, and the primed atoms labeled in brackets are generated by symmetry.

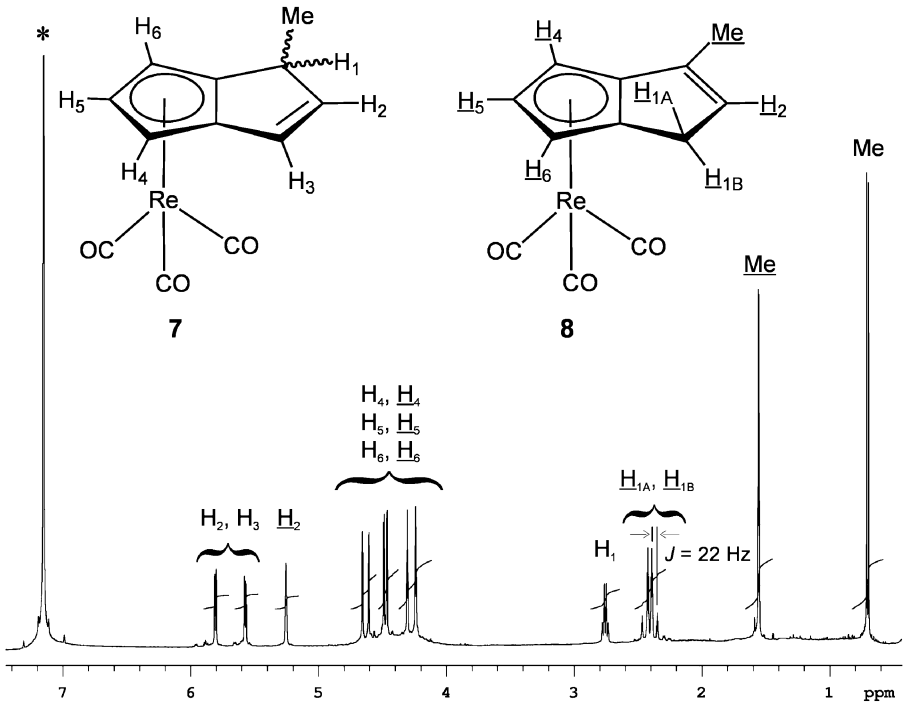
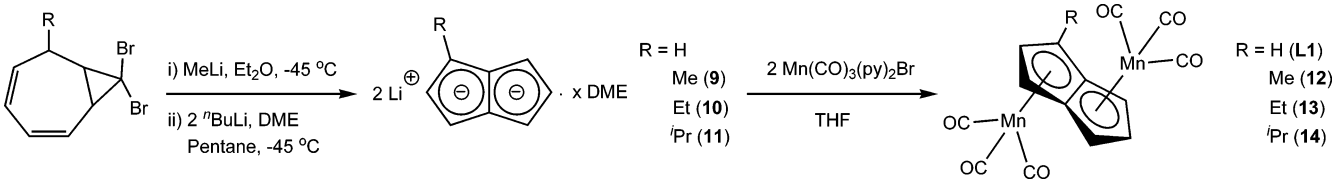


Figure 5. ^{1}H NMR spectrum (500 MHz) of isomers Re(η^5-Pn^{1-Me}H)(CO)$_3$ and Re(η^5-Pn^{3-Me}H)(CO)$_3$ in C_6D_6. The residual protio solvent resonance is marked with an asterisk.

by attempted fractional crystallization or by chromatographic separation. Comparison of the ^{1}H (Figure 5) and ^{13}C NMR spectra with those obtained for **6** allows identification of these isomers as Re(η^5-Pn^{1-Me}H)(CO)$_3$ (**7**) and Re(η^5-Pn^{3-Me}H)(CO)$_3$ (**8**), as outlined below. Three olefinic resonances (corresponding to the uncoordinated ring) are observed in the ^{1}H NMR spectrum (500 MHz) alongside six Cp-like resonances (shifted upfield from those of the Tl derivatives upon complexation to Re(CO)$_3$), demonstrating that the unsubstituted ring is coordinated to the Re center in both cases. The Me group at higher field appears as a doublet (J = 8 Hz) coupled to a quartet of triplets (J = 8 Hz, 2 Hz), confirming the presence of the 1-Me isomer **7**. Unfortunately, it was not possible to determine if this Me group has exo or endo geometry with regard to the Re(CO)$_3$ unit by using the aromatic solvent-induced shift (ASIS) method;[34] $\Delta\delta_{ASIS}$ values for the Me and H$_1$ resonances were very similar ($\Delta\delta_{ASIS}$ = 0.57 and 0.53 ppm, respectively). The characteristic AB quartet centered at ca. 2.4 ppm shows that the remaining

Scheme 2



isomer, **8**, has two strongly coupled, inequivalent protons as for **6**; the ^{13}C chemical shift observed for the quaternary carbon in the uncoordinated ring (134.1 ppm) exposes the site of alkylation to be the 3-position rather than the 2-position.[35] Hence, the constitution of isomers **4** and **5** in the starting mixture (Figure 3) is deduced (assuming no isomerization of the Me position or proton exchange between substituted and unsubstituted rings upon formation of **7** and **8**). Interestingly, the H_1 protons do not appear as an AB quartet in the ^{1}H NMR spectrum of isomer **5**, indicating that thallium−ring bonding is significantly ionic and/or fluxional in solution at room temperature.[27]

It is therefore concluded that the rearrangement of 8,8-dibromo-6-methylbicyclo[5.1.0]octa-2,4-diene gives methyl-substituted dihydropentalenes; monodeprotonation of these with TlOEt takes place exclusively at the unsubstituted ring to give a mixture of $Tl Pn^{1-Me}H$ and $Tl Pn^{3-Me}H$. The observed isomer distribution is consistent with the mechanism of 8,8-dibromobicyclo[5.1.0]octa-2,4-diene rearrangement outlined in Figure 2, whereby substitution at the 1-position in the starting material cannot give 2-substituted dihydropentalenes; 3-substituted dihydropentalenes may be generated, however, as a result of 1,5-H shifts in the initially formed 1-substituted dihydropentalenes.

1-Alkylpentalenyl Complexes. Twofold deprotonation of dihydropentalenes affords the 10-π-aromatic pentalenyl dianion; double deprotonation may be driven to effective completion by the use of 2 equiv of ^{n}BuLi in the presence of complexing ligands such as DME[15,36] and TMEDA.[37] Treatment of **1**−**3** with MeLi at −45 °C followed by extraction of the dihydropentalenes generated and their subsequent reaction with 2 equiv of ^{n}BuLi-DME gave the Li_2Pn^{1-R}·x DME salts (R = Me (**9**), R = Et (**10**), ^{i}Pr (**11**), respectively) as pyrophoric gray powders; the number of resonances observed in their respective ^{1}H NMR spectra suggested that only the 1-substituted isomer was present in each case, consistent with results for the methylhydropentalenyl species described above.

Reaction of **9**−**11** with 2 equiv of $Mn(CO)_3(py)_2Br$ afforded the dinuclear organometallic complexes *anti*-$[Mn(CO)_3]_2(\mu,\eta^5{:}\eta^5\text{-}Pn^{1-R})$ (R = Me (**12**), Et (**13**), ^{i}Pr (**14**), respectively; Scheme 2) as orange, crystalline solids which were fully characterized.

Table 2. Electrochemical Data[a] for 12−14 alongside Comparative Data for L1[8]

	L1	12	13	14
$E_{1/2}(1)$/V	− 1.91	− 1.93	− 1.91	− 1.90
$E_{1/2}(2)$/V	− 2.32	− 2.35	− 2.37	− 2.36

[a] All values were determined in THF/0.1 M $[^nBu_4N]^+[PF_6]^-$ at a scan rate of 50 mV s^{-1}, relative to the ferrocenium/ferrocene couple at 0.00 V.

Qualitatively, these complexes exhibit greater solubility in common organic solvents than their unsubstituted analogue, **L1**: for example, dissolving in pentanes to a limited degree. Two carbonyl resonances are discernible in the ^{13}C NMR spectra of **12**−**14**, presumably corresponding to separate signals from the $Mn(CO)_3$ groups coordinated to the alkylated and nonalkylated rings. **12**−**14** each display two quasi-reversible reductions by cyclic voltammetry at potentials very similar to those found for **L1** (Table 2), showing that monoalkylation perturbs the electronic nature of the complex only to a small extent.[38]

Single crystals of **12**−**14** suitable for X-ray diffraction analysis were grown by slow evaporation of Et_2O solutions; their structures are shown in Figure 6 and important bond lengths given in Table 1 along with comparative data for the unsubstituted complex, **L1**. Evidently, the alkyl group is present in the 1-position in all cases. The Pn^{1-R} ligands are facially enantiotopic, and crystals of **12**−**14** are each obtained as a racemic mixture of the two possible enantiomers (all complexes crystallize in centrosymmetric space groups). **12**−**14** display anti-$\mu,\eta^5{:}\eta^5$ coordination by the Pn^{1-R} ligand with an essentially planar pentalene ring system, as seen for **L1**.[8] A small degree of bond length deformation is observed for the alkylated rings: most significantly, the C1−C7 bond is lengthened due to the steric influence of the alkyl group; this is not seen for the unsubstituted rings. Concomitant sharpening of ∠C2−C1−C7 and widening of ∠C1−C2−C3 is observed for the substituted five-membered rings. The bond lengths and angles for the alkyl substituents are typical for an sp^3 carbon, and for **13** and **14** the α-carbon−carbon bonds of the alkyl groups are bent toward the Mn1 center**.** The $Mn-C_{ring}$, $Mn-C_O$, and C−O distances are similar for Mn1 and Mn2 in each complex and also when they are compared across the series; any differences are minimal and are best ascribed to crystal-packing influences. ^{1}H NMR spectra of the crude reaction mixtures of **12**−**14** reveal the presence of only one constitutional isomer in each case (the same isomer obtained upon workup and crystallization), and hence this crystallographic study shows that rearrangement of 8,8-dibromo-6-alkylbicyclo[5.1.0]octa-2,4-dienes and subsequent double deprotonation allows preparation of pentalenyl dianions substituted in the 1-position exclusively.

Conclusions

We have described a straightforward, easily modifiable route to 1-alkylpentalene ligands from the rearrangement of 8,8-dibromo-6-alkylbicyclo[5.1.0]octa-2,4-dienes when R is Me, 1°

(34) (a) Lamarche, J.-M.; Vebrel, J.; Laude, B. *Spectrochim. Acta* **1979**, *25A*, 673−677. (b) Ustynyuk, N. A.; Novikova, L. N.; Bel'skii, V. K.; Ofprunenko, Y. F.; Malyugina, S. G.; Trifonova, O. I.; Ustynyuk, Y. A. *J. Organomet. Chem.* **1985**, *294*, 31−44.

(35) $Cr(\eta^6\text{-indene})(CO)_3$ complexes of 2- and 3-methylindene are easily distinguished by the ^{13}C chemical shift of the quaternary C in the uncoordinated ring (156.2 and 138.0 ppm, respectively): Trifonova, O. I.; Ochertyanova, E. A.; Akhmedov, N. G.; Roznyatovsky, V. A.; Laikov, D. N.; Ustynyuk, N. A.; Ustynyuk, Y. A. *Inorg, Chim. Acta* **1998**, *280*, 328−338. Similarly, the quaternary olefinic ^{13}C resonances of 2- and 3-methylindene are observed at 145.9 and 139.9 ppm, respectively: Edlund, U. *Org. Magnet. Reson.* **1978**, *11*, 816−819. The chemical shift observed for C_3 in $Fe(\eta^5\text{-}Pn^{3-Ferrocenyl}H)(\eta^5\text{-Cp})$ is 133.4 ppm: Klimova, E. I.; Garcia, M. M.; Klimova, T.; Stivalet, J. M. M.; Ortega, S. H.; Ramirez, L. R. *J. Organomet. Chem.* **2002**, *659*, 56−63. ^{13}C resonances for the quaternary C atoms of 2-methyl-1,5-dihydropentalene occur to low field of 150 ppm.[13]

(36) Stezowski, J. J.; Hoier, H.; Willhelm, D.; Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1985**, 1263−1264.

(37) (a) Wilhelm, D.; Courtneidge, J. L.; Clark, T.; Davies, A. G. *J. Chem. Soc., Chem. Commun.* **1984**, 810−811. (b) Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *Organomet. Synth.* **1986**, *3*, 358−360.

(38) Lu, S.; Strelets, V. V.; Ryan, M. F.; Pietro, W. J.; Lever, A. B. P. *Inorg. Chem.* **1996**, *35*, 1013−1023.

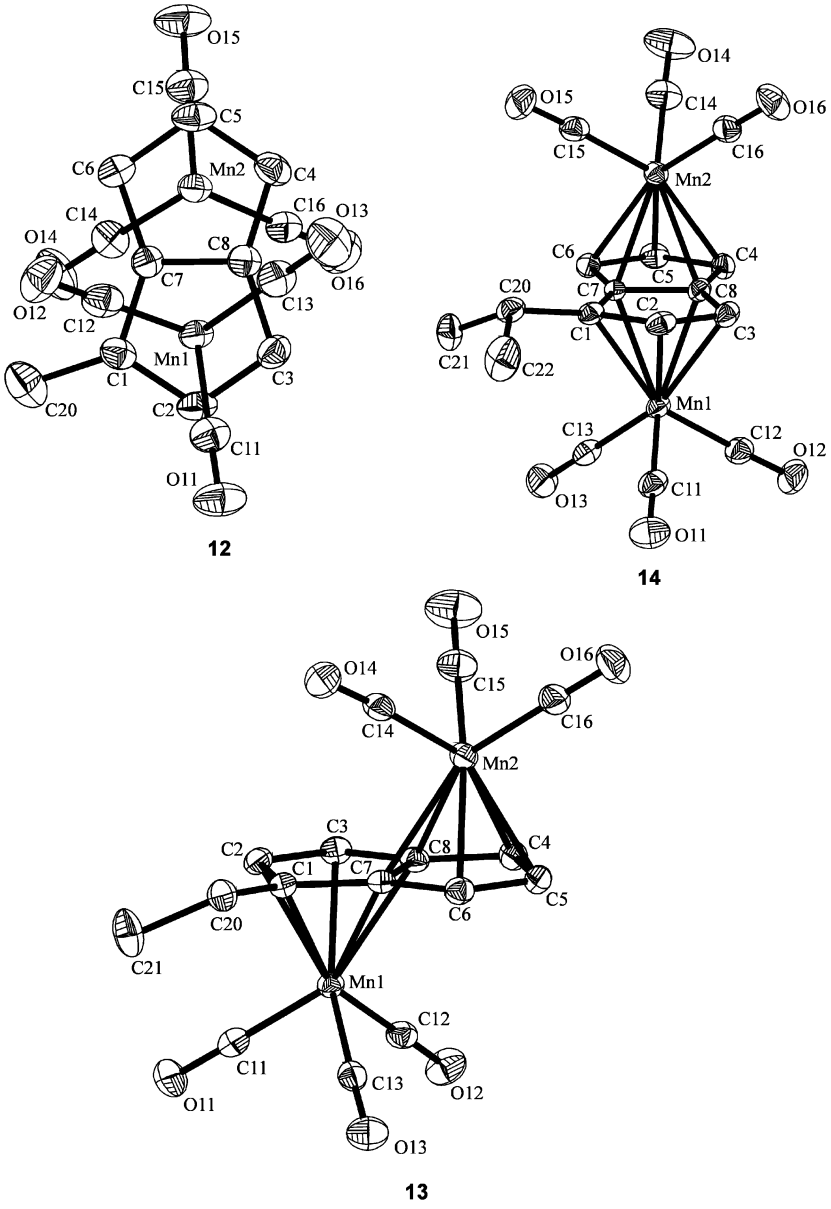


Figure 6. Crystal structures of *anti*-$[Mn(CO)_3]_2(\mu,\eta^5{:}\eta^5\text{-}Pn^{1-Me})$ (top view), *anti*-$[Mn(CO)_3]_2(\mu,\eta^5{:}\eta^5\text{-}Pn^{1-Et})$ (side view) and *anti*-$[Mn(CO)_3]_2(\mu,\eta^5{:}\eta^5\text{-}Pn^{1-iPr})$ (front view). Thermal ellipsoids are at the 50% probability level, and all H atoms are omitted for clarity.

alkyl (Et), or 2° alkyl (^{i}Pr). The synthesis affords hydropentalenyl and pentalenyl salts in good yield and is conveniently performed in solution. We anticipate that these ligands should find utility in future syntheses toward solubilized metal−pentalene oligomers, and investigations are currently in progress.[39]

Experimental Section

Caution! Thallium and its compounds are toxic and should be handled with caution using appropriate safety procedures. Contact with skin and inhalation of dust should be avoided; wastes should be collected and disposed of separately as heavy metal waste.

Reagents and Conditions. Where noted, reactions were performed under an inert atmosphere of dinitrogen utilizing standard Schlenk techniques or in a Vacuum Atmospheres glovebox. Solvents for oxygen- and water-sensitive reactions were dried by reflux over the appropriate drying agent (sodium−potassium alloy for pentane, potassium for THF and DME, sodium−benzophenone for Et_2O), distilled under a flowing stream of dinitrogen and stored in flame-dried ampules under a dinitrogen atmosphere; these were thoroughly degassed before use by passage of a stream of dinitrogen through the solvent. Otherwise, reactions were carried out in air using solvents obtained from standard sources that were used without further purification. Cycloheptatriene (90%), bromoform (96%), potassium *tert*-butoxide (95%), methyllithium (complex with lithium bromide, 1.5 M in Et_2O), *n*-butyllithium (2.5 M in hexanes), and thallium ethoxide (98%) were supplied by Aldrich and used without further purification. 7-Alkylcycloheptatrienes (R = methyl, ethyl, isopropyl, *tert*-butyl),[40] 8,8-dibromobicyclo[5.1.0]octa-2,4-diene,[41] $[Re(CO)_3(THF)Br]_2$[42] and $Mn(CO)_3(py)_2Br$[43] were prepared by the literature procedures.

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded using a Varian Unity Plus 500 MHz spectrometer, a Varian Mercury VX-

(39) Preliminary results suggest that $Fe(\eta^5\text{-}Pn^{Me}H)_2$ is formed as a complex mixture of isomers by reaction of **4** and **5** with $FeCl_2$·1.5THF.

(40) (a) Conrow, K. *J. Am. Chem. Soc.* **1961**, *83*, 2343−2350. (b) Picotin, G.; Faye, A.; Miginiac, P. *Bull. Soc. Chim. Fr.* **1990**, *127*, 245−251.

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(42) Storhoff, B. N.; Lewis, H. C. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 467−475.

(43) Abel, E. W.; Wilkinson, G. *J. Chem. Soc. A* **1959**, 1501−1505.

Works 300 MHz spectrometer, or a Varian Venus 300 MHz spectrometer. These were referenced via the residual protio solvent peak; chemical shifts (δ) are reported in parts per million (ppm) relative to TMS. Oxygen- or water-sensitive samples were prepared using dried solvents under a dinitrogen atmosphere in a glovebox and were sealed in tubes fitted with Young's type concentric stopcocks; solvents for NMR spectroscopy of oxygen- or water-sensitive materials were dried by reflux over the appropriate drying agent **(**potassium for C_6D_6, calcium hydride for C_5D_5N) and purified by trap-to-trap distillation. Elemental analyses were performed by the analytical department of the Inorganic Chemistry Laboratory, University of Oxford. Electron impact (EI) mass spectra were recorded by the mass spectrometry service, Inorganic Chemistry Laboratory, University of Oxford. High-resolution mass spectra were recorded on a GCT Micromass instrument calibrated with FC43, operating in electron impact mode with temperature-controlled addition to a solid probe. Fourier transform infrared spectra are reported in cm^{-1} and were recorded using a Perkin-Elmer FT1710 spectrometer (range 4000−400 cm^{-1}) as solids dispersed in KBr pellets or as thin films (made by evaporation of solutions) or Nujol mulls between KBr plates. Cyclic voltammograms were recorded on a CH Instruments potentiostat using a glassy-carbon working electrode with platinum-wire auxiliary and pseudo-reference electrodes. Measurements were made on deoxygenated THF solutions ca. 5×10^{-4} M in sample and 0.1 M in $[^nBu_4N]^+[PF_6]^-$ as supporting electrolyte. THF was freshly distilled before use. Potentials were referenced to the ferrocenium/ferrocene couple at 0.00 V by addition of ferrocene to the cell. The reversibility of the redox couple was judged by comparison with the behavior of the ferrocenium/ferrocene couple under the same conditions.

Synthesis of 8,8-Dibromo-6-alkylbicyclo[5.1.0]octa-2,4-diene (R = Me (1), Et (2), ^{i}Pr (3)). The method is described for **1**: a stirred solution of 7-methylcycloheptatriene (10.15 g, 95.59 mmol) and bromoform (24.16 g, 95.59 mmol) in pentanes (100 mL) was cooled to 0 °C. Solid KO^{t}Bu (13.50 g, 120.30 mmol) was added over a period of 10 min, taking care to maintain the temperature at 0 °C. The resulting brown mixture was warmed to room temperature and stirred overnight, after which the suspension was filtered through Celite on a sintered-glass frit. The clear orange-brown filtrate was washed with water (3×50 mL) and the washings back-extracted with pentanes; the combined pentane extracts were dried over $MgSO_4$, and volatiles were removed by rotary evaporation. Distillation of the residue under reduced pressure afforded 8,8-dibromo-6-methylbicyclo[5.1.0]octa-2,4-diene (**1**). Syntheses of **2** and **3** are analogous and were achieved by substituting the respective 7-alkylcycloheptatriene, using the same stoichiometric amounts of reagents; **1**−**3** were obtained as viscous pale yellow oils after distillation.

Data for 8,8-dibromo-6-methylbicyclo[5.1.0]octa-2,4-diene (**1**) are as follows. Bp: 42−48 °C (0.1 mbar). Yield: 4.06 g, 14.60 mmol, 15%. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 5.81 (m, 1H), 5.60 (m, 1H), 5.56 (m, 1H), 5.44 (m, 1H), 2.62 (m (br), 1H), 1.91 (m, 1H), 1.73 (m, 1H), 0.94 (d, $J = 7$ Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 300 K): δ 140.3 (*C*H), 130.8 (*C*H, 2 overlapping resonances), 126.3 (*C*H), 46.0 (*C*H), 35.0 (*C*H), 33.9 (*C*H), 31.4 (*C*Br$_2$), 19.3 (*C*H$_3$). Anal. Calcd for $C_9H_{10}Br_2$ (mol wt 277.98): C, 38.90; H, 3.60. Found: C, 39.03; H, 3.70. MS (EI): *m*/*z* 278 ([M]$^+$, 4%), 199 ([M − Br]$^+$, 12%), 118 ([M − 2Br]$^+$, 100%). IR (thin film): 3018 (s), 2960 (s), 2928 (m), 2870 (m), 1608 (w), 1454 (m), 1372 (m), 1254 (m), 1200 (m), 1162 (m), 1072 (s), 1008 (m), 800 (s), 772 (m), 744 (s), 686 (vs), 658 (s).

Data for 8,8-dibromo-6-ethylbicyclo[5.1.0]octa-2,4-diene (**2**) are as follows. Bp: 64−68 °C (0.1 mbar). Yield: 1.55 g, 5.31 mmol, 9%. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 5.81 (m, 1H), 5.63 (m, 1H), 5.60 (m, 1H), 5.50 (m, 1H), 2.45 (m (br), 1H), 1.95 (m, 1H), 1.71 (m, 1H), 1.34 (m of q, $J = 7$ Hz, 2H), 0.94 (t, $J = 7$ Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 300 K): δ 139.1 (*C*H), 130.8 (*C*H, 2 overlapping resonances), 126.6 (*C*H), 45.1 (*C*H), 41.2 (*C*H), 33.7 (*C*H), 33.0 (*C*Br$_2$), 28.3 (*C*H$_2$), 12.2 (*C*H$_3$). Anal. Calcd for $C_{10}H_{12}Br_2$ (mol wt 292.01): C, 41.13; H, 4.14. Found: C, 41.09; H, 4.03. MS (EI): *m*/*z* 292 ([M]$^+$, 2%), 213 ([M − Br]$^+$, 12%), 132 ([M − 2Br]$^+$, 100%). IR (thin film): 3016 (s), 2960 (vs), 2928 (s), 2874 (m), 2856 (m), 1632 (w), 1588 (m), 1460 (s), 1382 (m), 1254 (m), 1242 (w), 1200 (m), 1156 (w), 1068 (s), 1022 (m), 898 (m), 846 (w), 814 (m), 780 (m), 744 (s), 688 (vs), 658 (s), 578 (m), 496 (s).

Data for 8,8-dibromo-6-isopropylbicyclo[5.1.0]octa-2,4-diene (**3**) are as follows. Bp: 30−32 °C (0.1 mbar). Yield: 2.89 g, 9.44 mmol, 9%. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ 5.81 (m, 1H), 5.79 (m, 1H), 5.71 (m, 1H), 5.68 (m, 1H), 2.32 (m (br), 1H), 1.92 (m, 1H), 1.77 (m, 1H), 1.48 (sept of m, $J = 7$ Hz, 1H), 0.98 (d, $J = 7$ Hz, 3H), 0.82 (d, $J = 7$ Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 300 K): δ 138.1 (*C*H), 130.8 (*C*H), 130.7 (*C*H), 126.7 (*C*H), 45.9 (*C*H), 44.0 (*C*H), 33.8 (*C*Br$_2$), 33.5 (*C*H), 32.5 (*C*H), 20.9 (*C*H$_3$), 20.3 (*C*H$_3$). Anal. Calcd for $C_{11}H_{14}Br_2$ (mol wt 306.04): C, 43.17; H, 4.61. Found: C, 43.27; H, 4.34. MS (EI): *m*/*z* 306 ([M]$^+$, 8%), 291 ([M − Me]$^+$, 15%), 146 ([M − 2Br]$^+$, 42%), 131 ([M − 2Br − Me]$^+$, 100%). IR (thin film): 3018 (s), 2958 (s), 2928 (s), 2872 (s), 1640 (w), 1612 (w), 1464 (s), 1388 (s), 1370 (s), 1338 (w), 1250 (m), 1202 (m), 1172 (m), 1076 (s), 1046 (s), 1008 (m), 958 (w), 916 (m), 900 (m), 846 (m), 808 (s), 770 (s), 746 (s), 690 (s), 656 (s), 592 (m), 576 (m), 500 (m).

Synthesis of TlPnH. A stirred solution of 8,8-dibromobicyclo-[5.1.0]octa-2,4-diene (6.94 g, 26.29 mmol) in dry Et$_2$O (30 mL) under dinitrogen was cooled to −45 °C (dry ice/acetonitrile bath). A solution of MeLi (1.5 M in Et$_2$O, 17.6 mL, 26.40 mmol) was added dropwise over a period of 10 min and the resulting solution stirred for a further 10 min. Volatiles were removed in vacuo (0.1 mbar) at −45 °C, and the resulting thick paste was extracted with cold dry pentanes (−45 °C, 5×10 mL) using a filter cannula. Addition of TlOEt (1.87 mL, 26.40 mmol) to the filtrate at −45 °C resulted in the formation of a yellow precipitate. The suspension was warmed to room temperature and stirred overnight in the absence of light. The resulting bright yellow solid, TlPnH, was collected by filtration, washed with dry pentanes (5×10 mL), dried in vacuo, and stored under dinitrogen in the absence of light. *Note*: TlPnH is *light sensitive*, decomposing to dark material upon prolonged exposure. Yield: 4.69 g, 15.25 mmol, 58%. ^{1}H NMR data were in accord with the literature data.[28]

Synthesis of TlPn^{1-Me}H (4) and TlPn^{3-Me}H (5). A procedure identical with that described for TlPnH above was followed with stoichiometric substitution of **1** for 8,8-dibromobicyclo[5.1.0]octa-2,4-diene. A mixture of TlPn^{1-Me}H (**4**) and TlPn^{3-Me}H (**5**) was obtained as an air-sensitive, bright yellow solid and stored under dinitrogen in the absence of light. *Note*: **4** and **5** are *light sensitive*, decomposing to dark material upon prolonged exposure. Combined yield: 1.40 g, 4.35 mmol, 70%. ^{1}H NMR (300 MHz, C_5D_5N, 300 K): TlPn^{1-Me}H, δ 6.66 (m, 1H), 6.09 (m, 1H), 6.07 (m, 1H), 5.94 (m, 1H), 5.71 (m, 1H), 3.00 (q of m, $J = 7$ Hz, 1H), 1.24 (d, $J = 7$ Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, C_5D_5N, 300 K): TlPn^{1-Me}H, δ 138.2 (*C*H), 126.5 (*C*H), 107.0 (*C*H), 101.6 (*C*H), 96.5 (*C*H), 40.0 (*C*H), 20.9 (*C*H$_3$). ^{1}H NMR (300 MHz, C_5D_5N, 300 K): TlPn^{3-Me}H, δ 6.14 (m, 1H), 5.99 (m, 1H), 5.83 (m, 1H), 5.76 (m, 1H), 2.84 (m, 2H), 2.14 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, C_5D_5N, 300 K): TlPn^{3-Me}H, δ 125.9 (*C*H), 107.3 (*C*H), 102.5 (*C*H), 95.6 (*C*H), 33.2 (*C*H$_2$), 14.8 (*C*H$_3$). MS (EI): *m*/*z* 322 ([M]$^+$, 43%), 205 ([Tl]$^+$, 100%), 117 ([C_9H_9]$^+$, 26%). HRMS (EI) found (calcd for ^{205}Tl): 322.0463 (322.0448). IR (Nujol mull): 1541 (m), 1377 (s), 1350 (m), 1308 (m), 1288 (w), 1119 (s), 1062 (s), 1050 (m), 1015 (m), 721 (vs), 668 (s).

Synthesis of Re(η^5-PnH)(CO)$_3$ (6). A suspension of [Re(CO)$_3$-(THF)Br]$_2$ (1.00 g, 1.19 mmol) and TlPnH (0.73 g, 2.37 mmol) in dry THF (50 mL) was stirred in the absence of light for 48 h. Volatiles were removed in vacuo, and the cream-colored residue

was extracted with toluene (3 × 30 mL) in air, the extracts were filtered through Celite, and the resultant pale yellow solution was evaporated to dryness. The product was purified by flash chromatography (silica, $CHCl_2$ elution), and the colorless fraction collected was evaporated to dryness to give Re(η^5-PnH)$(CO)_3$ (**6**) as a crystalline white solid. Yield: 0.53 g, 1.42 mmol, 60%. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ 5.88 (d of t, J = 6 Hz, 2 Hz, 1H), 5.59 (d of t, J = 6 Hz, 2 Hz, 1H), 4.60 (d, J = 2 Hz, 1H), 4.52 (d, J = 2 Hz, 1H), 4.26 (t, J = 2 Hz, 1H), 2.42 (d of t, J = 22 Hz, 2 Hz, 1H), 2.26 (d of t, J = 22 Hz, 2 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 300 K): δ 195.5 (*C*O), 138.3 (*C*H), 124.5 (*C*H), 117.6 (*C* quat), 111.0 (*C* quat), 83.8 (*C*H), 78.4 (*C*H), 73.8 (*C*H), 34.0 (CH_2). Anal. Calcd for $C_{11}H_7O_3Re$ (mol wt 373.38): C, 35.39; H, 1.89. Found: C, 35.47; H, 1.91. MS (EI): *m*/*z* 374 ([M]$^+$, 78%), 346 ([M − CO]$^+$, 10%), 318 ([M − 2CO]$^+$, 87%), 290 ([M − 3CO]$^+$, 100%). IR (KBr, ν_{CO}): 2016 (s), 1900 (s).

Synthesis of Re(η^5-Pn^{1-Me}H)$(CO)_3$ (7) and Re(η^5-Pn^{3-Me}H)$(CO)_3$ (8). A suspension of the isomer mixture of **4** and **5** (0.40 g, 1.24 mmol) and $[Re(CO)_3(THF)Br]_2$ (0.53 g, 0.63 mmol) in dry THF (50 mL) under dinitrogen was stirred in the absence of light for 48 h. Volatiles were removed in vacuo, and the cream-colored residue was extracted with toluene (3 × 30 mL) in air, the extracts were filtered through Celite, and the resultant pale yellow solution was evaporated to dryness. The product was purified by flash chromatography (silica, CH_2Cl_2 elution), and the pale yellow fraction collected was evaporated to dryness to give a mixture of Re(η^5-Pn^{1-Me}H)$(CO)_3$ (**7**) and Re(η^5-Pn^{3-Me}H)$(CO)_3$ (**8**), as a thick yellow oil. Combined yield: 0.32 g, 0.83 mmol, 67%. ^{1}H NMR (500 MHz, C_6D_6, 300 K): both isomers, δ 5.80 (d of d, J = 6 Hz, 2 Hz, 1H), 5.57 (d of d, J = 6 Hz, 2 Hz, 1H), 5.25 (m, 1H), 4.66 (d, J = 2 Hz, 1H), 4.61 (d, J = 2 Hz, 1H), 4.49 (d, J = 2 Hz, 1H), 4.47 (d, J = 2 Hz, 1H), 4.30 (t, J = 2 Hz, 1H), 4.24 (d, J = 2 Hz, 1H), 2.76 (q of t, J = 8 Hz, 2 Hz, 1H), 2.47 (d of m, J = 22 Hz, 1H), 2.35 (d of m, J = 22 Hz, 1H), 1.56 (m, 3H), 0.70 (d, J = 8 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K): both isomers, δ 196.7 (*C*O), 145.1 (*C*H), 134.1 (*C* quat), 132.3 (*C*H), 122.8 (*C*H), 119.3 (*C* quat), 116.8 (*C* quat), 115.3 (*C* quat), 111.4 (*C* quat), 83.4 (*C*H), 82.6 (*C*H), 77.3 (*C*H), 77.1 (*C*H), 73.7 (*C*H), 71.0 (*C*H), 39.7 (*C*H), 31.7 (CH_2), 15.5 (CH_3), 11.6 (CH_3). MS (EI): *m*/*z* 388 ([M]$^+$, 44%), 332 ([M − 2CO]$^+$, 64%), 302 ([M − 3CO]$^+$, 100%). High-resolution MS (EI) found (calcd for ^{187}Re): 388.0124 (388.0109). IR (thin film, ν_{CO}): 2016 (s), 1908 (s).

Synthesis of Li_2Pn·*x*DME. A stirred solution of 8,8-dibromobicyclo[5.1.0]octa-2,4-diene (4.54 g, 17.20 mmol) in dry Et_2O (30 mL) under dinitrogen was cooled to −45 °C (dry ice/acetonitrile bath). A solution of MeLi (1.5 M in Et_2O, 11.5 mL, 17.25 mmol) was added dropwise over a period of 10 min and the resulting solution stirred for a further 10 min. Volatiles were removed in vacuo (0.1 mbar) at −45 °C, and the resulting thick paste was extracted with cold dry pentanes (−45 °C, 5 × 10 mL) using a filter cannula. Dry DME (3.6 mL, 34.63 mmol) was added to the cold filtrate, after which ^{n}BuLi (2.5 M in hexanes, 13.8 mL, 34.50 mmol) was added dropwise. The suspension was warmed to room temperature and stirred overnight. The solid precipitate was collected by filtration on a sintered-glass frit, washed with dry pentanes (10 × 10 mL), and dried in vacuo for 6 h. This afforded Li_2Pn·*x*DME (x = 0.51) as an off-white powder that was stored under dinitrogen. The quantities of reagents used in the synthesis described are typical; x is generally found to vary between ca. 0.3 and 1.5 and may be determined by ^{1}H NMR spectroscopy using the relative integration values of the pentalene and DME peaks. Typical yield (Li_2Pn·*x*DME, x = 0.51): 2.30 g, 14.19 mmol, 83%. ^{1}H NMR (300 MHz, C_5D_5N, 300 K): δ 6.79 (t, J = 3 Hz, 2H), 6.10 (d, J = 3 Hz, 4H), 3.46 (s, 4H, DME), 3.24 (s, 6H, DME).

Synthesis of Li_2Pn^{1-R}·*x*DME; R = Me (9), Et (10), ^{i}Pr (11). A procedure identical with that described for Li_2Pn·*x*DME above was followed with stoichiometric substitution of **1**−**3**, respectively, for 8,8-dibromobicyclo[5.1.0]octa-2,4-diene; **9**−**11** were obtained as air-sensitive off-white powders that were stored under dinitrogen.

Data for Li_2Pn^{1-Me}·*x*DME (**9**) are as follows. Yield: 2.89 g, 10.70 mmol, 61% (x = 1.55). ^{1}H NMR (500 MHz, C_5D_5N, 300 K): δ 6.75 (m, 1H), 6.47 (m, 1H), 6.29 (m, 1H), 6.24 (m, 1H), 6.01 (m, 1H), 3.46 (s, 4H, DME), 3.24 (s, 6H, DME), 2.26 (s, 3H).

Data for Li_2Pn^{1-Et}·*x*DME (**10**) are as follows. Yield: 0.68 g, 4.24 mmol, 70% (x = 0.18). ^{1}H NMR (300 MHz, C_5D_5N, 300 K): δ 6.79 (m, 1H), 6.49 (m, 1H), 6.27 (m, 1H), 6.24 (m, 1H), 6.04 (m, 1H), 3.48 (s, 4H, DME), 3.24 (s, 6H, DME), 2.55 (m of q, J = 7 Hz, 2H), 1.25 (t, J = 7 Hz, 3H).

Data for Li_2Pn^{1-iPr}·*x*DME (**11**) are as follows. Yield: 1.04 g, 5.01 mmol, 53% (x = 0.56). ^{1}H NMR (300 MHz, C_5D_5N, 300 K): δ 6.83 (m, 1H), 6.51 (m, 1H), 6.23 (m, 1H), 6.20 (m, 1H), 6.05 (m, 1H), 3.47 (s, 4H, DME), 3.24 (s, 6H, DME), 2.83 (sept., J = 7 Hz, 1H), 1.31 (d, J = 7 Hz, 3H), 1.30 (d, J = 7 Hz, 3H).

Synthesis of *anti*-$[Mn(CO)_3]_2(\mu,\eta^5{:}\eta^5$-Pn$^{1-R})$ (R = Me (12), Et (13), ^{i}Pr (14)). The method is described for **12**: a suspension of **9** (0.50 g, 1.85 mmol) in dry THF (30 mL) under dinitrogen was added dropwise to a stirred suspension of $Mn(CO)_3(py)_2Br$ (1.40 g, 3.71 mmol) in dry THF (30 mL) at −78 °C, producing a red solution. This was warmed to room temperature and stirred for 1 h before volatile materials were removed in vacuo to give an orange-brown solid. This residue was extracted with toluene (2 × 30 mL) in air, the extracts were filtered through Celite, and the resulting red solution was evaporated to dryness, yielding an orange solid which was shown to contain a small amount of $Mn(CO)_3(py)_2Br$ starting material by ^{1}H NMR spectroscopy. The product was purified by flash chromatography (silica, CH_2Cl_2/hexanes (9:1) elution), and the orange fraction collected was evaporated to dryness to give *anti*-$[Mn(CO)_3]_2(\mu,\eta^5{:}\eta^5$-Pn$^{1-Me})$ (**12**). Syntheses of **13** and **14** are analogous and were achieved by substituting lithium salts **10** and **11**, respectively, using the same stoichiometric amounts of reagents; **12**−**14** were obtained as crystalline orange solids.

Data for *anti*-$[Mn(CO)_3]_2(\mu,\eta^5{:}\eta^5$-Pn$^{1-Me})$ (**12**) are as follows. Yield: 0.50 g, 1.27 mmol, 69%. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ 4.06 (m, 2H), 3.89 (d, J = 3 Hz, 1H), 3.73 (t, J = 3 Hz, 1H), 3.67 (d, J = 3 Hz, 1H), 1.74 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 300 K): δ 223.0 (*C*O), 222.5 (*C*O), 96.3 (*C*H), 95.5 (*C*H), 85.2 (*C* quat.), 84.6 (*C* quat), 83.6 (*C* quat), 66.0 (*C*H), 64.7 (*C*H), 62.6 (*C*H), 13.3 (CH_3). Anal. Calcd for $C_{15}H_8Mn_2O_6$ (mol wt 394.10): C, 45.72; H, 2.05. Found: C, 45.15; H, 2.22. MS (EI): *m*/*z* 394 ([M]$^+$, 18%), 366 ([M − CO]$^+$, 25%), 338 ([M − 2CO]$^+$, 34%), 310 ([M − 3CO]$^+$, 28%), 282 ([M − 4CO]$^+$, 4%), 254 ([M − 5CO]$^+$, 82%), 226 ([M − 6CO]$^+$, 85%) 171 ([C_9H_8Mn]$^+$, 100%). IR (KBr, ν_{CO}): 2010 (s), 1924 (s). CV (THF, 0.1 M [^{n}Bu$_4$N]$^+$-[PF$_6$]$^-$): $E_{1/2}$ = −1.93 V, $E_{1/2}$ = −2.35 V (both quasi-reversible).

Data for *anti*-$[Mn(CO)_3]_2(\mu,\eta^5{:}\eta^5$-Pn$^{1-Et})$ (**13**) are as follows. Yield: 0.19 g, 0.47 mmol, 12%. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ 4.13 (m, 1H), 4.09 (m, 1H), 3.95 (m, 1H), 3.75 (m, 2H), 2.24 (d of q, J = 15 Hz, 7 Hz, 1H), 2.14 (d of q, J = 15 Hz, 7 Hz, 1H), 0.95 (t, J = 7 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 300 K): δ 223.5 (*C*O), 223.0 (*C*O), 95.3 (*C*H), 94.4 (*C*H), 90.5 (*C* quat), 84.8 (*C* quat), 84.1 (*C* quat), 65.7 (*C*H), 64.7 (*C*H), 62.6 (*C*H), 20.6 (CH_2), 14.0 (CH_3). Anal. Calcd for $C_{16}H_{10}Mn_2O_6$ (mol wt 408.12): C, 47.09; H, 2.47. Found: C, 47.17; H, 1.99. MS (EI): *m*/*z* 408 ([M]$^+$, 16%), 380 ([M − CO]$^+$, 25%), 352 ([M − 2CO]$^+$, 48%), 324 ([M − 3CO]$^+$, 50%), 296 ([M − 4CO]$^+$, 4%), 268 ([M − 5CO]$^+$, 95%), 240 ([M − 6CO]$^+$, 100%) 185 ([$C_{10}H_{10}$-Mn]$^+$, 85%). IR (KBr, ν_{CO}): 2008 (s), 1952 (s), 1928 (s). CV (THF, 0.1 M [^{n}Bu$_4$N]$^+$[PF$_6$]$^-$): $E_{1/2}$ = −1.91 V, $E_{1/2}$ = −2.37 V (both quasi-reversible).

Data for *anti*-$[Mn(CO)_3]_2(\mu,\eta^5{:}\eta^5$-Pn$^{1-iPr})$ (**14**) are as follows. Yield: 0.38 g, 0.90 mmol, 53%. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ 4.20 (m, 1H), 4.13 (m, 1H), 4.02 (m, 1H), 3.81 (m, 1H), 3.76 (m, 1H), 2.61 (sept, J = 7 Hz, 1H), 1.23 (d, J = 7 Hz, 3H),

Table 3. Crystallographic Details for 6 and 12−14

	6	12	13	14
formula	$C_{11}H_7O_3Re$	$C_{15}H_8Mn_2O_6$	$C_{16}H_{10}Mn_2O_6$	$C_{17}H_{12}Mn_2O_6$
formula wt	373.38	394.10	408.12	422.15
size/mm	0.2 × 0.2 × 0.1	0.2 × 0.1 × 0.1	0.3 × 0.2 × 0.2	0.4 × 0.4 × 0.1
cryst class	triclinic	triclinic	monoclinic	monoclinic
space group (No.)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P2_1/c$ (14)	$P2_1/c$ (14)
a/Å	6.0714(2)	6.7712(2)	6.86320(10)	17.4102(7)
b/Å	6.8277(3)	7.5109(3)	11.32190(10)	6.7355(2)
c/Å	12.4527(5)	16.5455(5)	20.2280(4)	14.2396(5)
α/deg	92.143(2)	88.334(2)	90	90
β/deg	90.633(2)	81.164(2)	91.8950(10)	96.0030(10)
γ/deg	101.523(2)	65.199(2)	90	90
V/Å^3	505.36(3)	754.21(5)	1570.95(4)	1660.67(10)
Z	2	2	4	4
D_{calcd}/g cm^{-3}	2.454	1.735	1.726	1.688
μ/mm^{-1}	12.003	1.700	1.636	1.551
F(000)	344	392	816	848
θ range/deg	5.22−27.57	5.35−27.52	5.13−27.46	5.27−27.48
total no. of data	4173	5342	6509	6770
no. of unique data	2285	3168	3531	3757
no. of obsd data ($I > 2\sigma(I)$)	2169	2705	3147	2910
final *R* indices[a]	R1 = 0.0276, wR2 = 0.0724	R1 = 0.0477, wR2 = 0.1087	R1 = 0.0245, wR2 = 0.0593	R1 = 0.0342, wR2 = 0.0767
GOF[b]	1.048	1.189	1.039	1.020
residual *ρ*/e Å^{-3}	1.755, −1.586	1.072, −0.605	0.344, −0.402	0.396, −0.451

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ ($I > 2\sigma(I)$). [b] $GOF = [\sum w(F_o^2 - F_c^2)^2/(M - N)]^{1/2}$, where *M* is the number of reflections and *N* is the number of parameters refined.

0.97 (d, $J = 7$ Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 300 K): *δ* 223.6 (*C*O), 223.1 (*C*O), 95.7 (*C*H), 95.2 (*C*H), 94.4 (*C* quat), 85.5 (*C* quat), 82.7 (*C* quat), 65.7 (*C*H, 2 overlapping resonances), 63.3 (*C*H), 26.9 (*C*H), 23.7 (*C*H$_3$), 22.7 (*C*H$_3$). Anal. Calcd for $C_{17}H_{12}Mn_2O_6$ (mol wt 422.15): C, 48.37; H, 2.87. Found: C, 48.34; H, 2.70. MS (EI): *m*/*z* 422 ([M]$^+$, 12%), 394 ([M − CO]$^+$, 12%), 366 ([M − 2CO]$^+$, 30%), 338 ([M − 3CO]$^+$, 42%), 282 ([M − 5CO]$^+$, 68%), 254 ([M − 6CO]$^+$, 100%) 199 ([$C_{11}H_{12}Mn$]$^+$, 35%). Infrared (KBr, ν_{CO}): 2006 (s), 1960 (s), 1920 (s). CV (THF, 0.1 M [^{n}Bu$_4$N]$^+$[PF$_6$]$^-$): $E_{1/2} = -1.90$ V, $E_{1/2} = -2.36$ V (both quasi-reversible).

X-ray Crystallography. Crystals of **6** and **12−14** suitable for an X-ray diffraction study were grown by slow evaporation of Et$_2$O solutions. These were mounted on glass fibers using perfluoropolyether oil, transferred to a goniometer head on the diffractometer, and cooled rapidly to 150(2) K under a stream of cold N_2 using an Oxford Cryostream 600 series instrument. Data collections were performed using an Enraf-Nonius FR590 Kappa CCD diffractometer utilizing Mo Kα X-ray radiation ($\lambda = 0.710\,73$ Å). The data were processed using the programs DENZO and SCALEPACK.[44] Structures were solved using the direct-methods program SHELXS[45] and refined using full-matrix least-squares refinement on all F^2 data using SHELX-97 in the WinGX package.[46] For all structures the heavy-atom positions were determined by direct methods; subsequent Fourier difference syntheses revealed the positions of the other non-H atomic sites. In general, all non-H sites were refined using anisotropic thermal parameters. H atoms were included in calculated positions and allowed to ride on their attached C atoms with isotropic thermal parameters (according to the atom to which they were attached); these were not refined. Crystal data and collection parameters are given in Table 3.

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Supporting Information Available: Crystallographic data for **6** and **12−14** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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