An Analogue of Cymantrene [(η^5-C_5H_5)Mn(CO)$_3$] That Contains a Dimetalladithiacyclopentadienyl ring**

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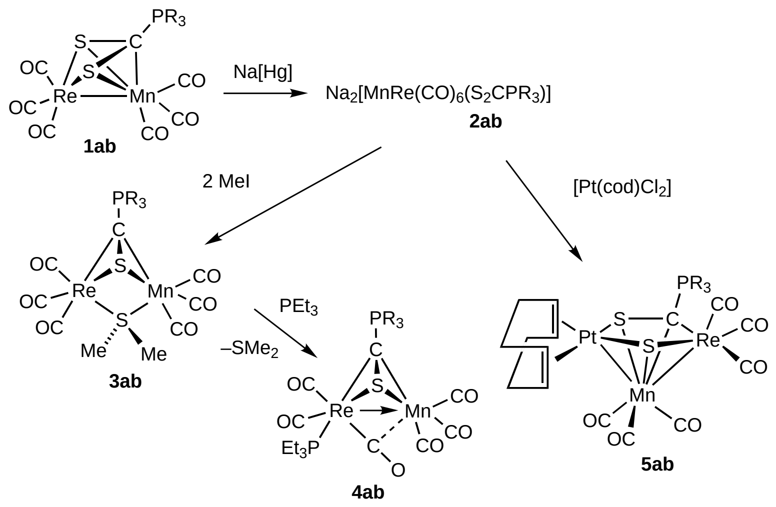
The discovery of metal complexes with aromatic rings as π-donors initiated a new age of organo-transition-metal chemistry.[1] Many complexes of this type, which bear heteroatom-substituted rings, are now known[2] and in the last decades metal-complexed metallaarenes[3] and metallahetero-atomarenes[4] have been prepared.

Metal π complexes of dimetallacycles have been reported by Chisholm et al.[5] and by Rothwell and co-workers.[6] The latter can be considered as metallaarenes, whereas the former show a severe distortion from planarity, which has been taken as indicative of non-aromatic character. This seems to be the current frontier in the transition from purely carbon-based rings to heteroatom- or metal-substituted rings as π ligands. We report herein the first example of a transition-metal π complex of a ring that contains two heteroatoms and two different transition metals.



Scheme 1. Preparation of **4** and **5**. **a**: R = *i*Pr, **b**: R = Cy.

We previously found that the reaction of dianions [MnRe(CO)$_6$(μ-S_2CPR_3)]$^{2-}$ (**2a**–**b**) with excess of NH_4PF_6 leads to C–S cleavage and double protonation.[7] Analogously, reaction of **2a**–**b** with excess MeI gave complexes **3a**–**b** (Scheme 1). Spectroscopic data support the structure depicted in Scheme 1, resulting from double methylation at the sulfur atom. Reaction of **3a**–**b** with PEt$_3$ afforded more stable derivatives **4a**–**b**. An X-ray determination of the structure of **4a** (Figure 1)[8] showed that the SMe$_2$ group had been substituted by Et$_3$P, and the presence of the thiocarbonyl-phosphorane ligand SCP*i*Pr$_3$.[9]

We speculated that C–S-bond breaking occurs in the reactions of **2a**–**b** with H$^+$ and Me$^+$ because electrons are required to create the new bond to H or Me groups, and that using a high-electron-count metal fragment as electrophile instead could result in bond formation without concomitant bond breaking. We found that **2a**–**b** react with [PtCl$_2$(cod)] (cod = cycloocta-1,5-diene) to yield the trimetallic derivatives **5a**–**b**. A molecule of **5a** (Figure 2)[10] contains an angular Pt-Mn-Re framework with Pt-Mn (2.956(1) Å) and Re-Mn (2.822(1) Å) distances consistent with metal–metal bonds.[11] Contrary to our expectation, C–S-bond breaking took place to give SCPR$_3$ and S ligands, both of which act as bridges between the three metal centers.

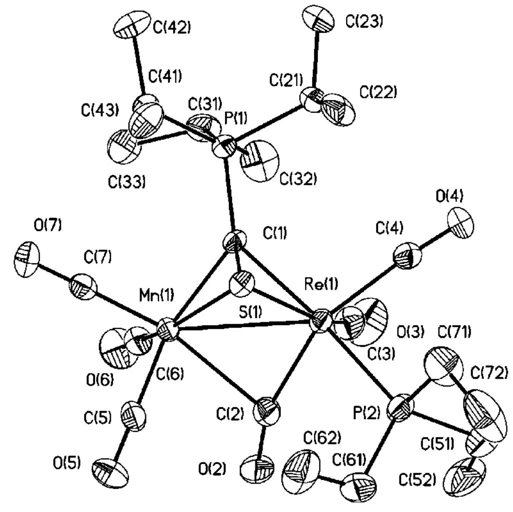


Figure 1. Molecular structure of **4a**: selected bond lengths [Å] and angles [°]: Re(1)-Mn(1) 2.7824(13), Re(1)-S(1) 2.4456(17), Re(1)-C(1) 2.138(6), Mn(1)-S(1) 2.310(2), Mn(1)-C(1) 2.009(7), Re(1)-C(2) 1.986(8), S(1)-C(1) 1.798(7), Mn(1)..C(2) 2.430(9), C(4)-Re(1)-C(2) 156.5(3), C(1)-Re(1)-P(2) 145.45(19), C(3)-Re(1)-S(1) 153.9(3), C(5)-Mn(1)-C(1) 155.1(3), C(6)-Mn(1)-S(1) 155.2(3).

The Pt-S(2)-C(1)-Re-S(1) ring is planar; the highest deviation occurs with Re(1), which is 0.115(3) Å out of plane. The Mn atom is bonded to all five atoms in the ring in a fairly symmetrical disposition. The plane formed by the carbon atoms of the three carbonyl groups bonded to Mn is virtually parallel to the Pt-S-C-Re-S ring (angle between planes 6.31°). All these geometrical features suggest that the structure of **5a** can be viewed as a dithiadimetallic analogue of cymantrene [Mn(η^5-C_5H_5)(CO$_3$)].[12] This can be rationalized by considering that all the fragments involved in the five-membered ring

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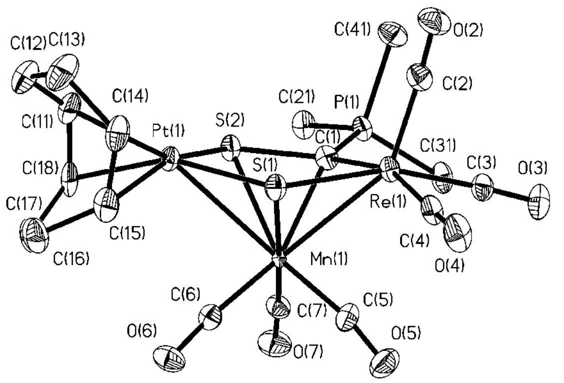

Figure 2. Molecular structure of **5a**: selected bond lengths [Å] and angles [°]: Pt(1)-S(2) 2.272(2), Pt(1)-S(1) 2.290(2), Pt(1)-Mn(1) 2.9563(13), Re(1)-C(1) 2.115(9), Re(1)-S(1) 2.428(2), Re(1)-Mn(1) 2.8216(13), Mn(1)-C(1) 2.220(10), Mn(1)-S(2) 2.426(3), Mn(1)-S(1) 2.479(3), S(2)-C(1) 1.803(10), S(2)-Pt(1)-S(1) 88.89(9), Pt(1)-S(1)-Re(1) 120.74(10), C(1)-Re(1)-S(1) 84.9(3), S(2)-C(1)-Re(1) 128.0(5), C(1)-S(2)-Pt(1) 115.4(3), Re(1)-Mn(1)-Pt(1) 90.42(4).

are isolobal with neutral or charged CH fragments.[13] The ring itself is thus isolobal with Cp, and the five metal atoms are able to donate a total of five electrons to the {$Mn(CO)_3$} fragment (13 electrons) to fulfil the 18-electron rule.

Complexes **5a**–**b** represent the highest degree of heavy-atom substitution (two transition-metal atoms and two sulfur atoms) in a metal π-complexed ring, and the first example of a dimetallacyclopentadiene with two different metal atoms.

Theoretical studies addressing the issue of aromaticity in **5a**–**b**, as well as attempts to liberate the {$Mn(CO)_3$} fragment will be pursued.

Experimental Section

3a: CH_3I (39 μL, 0.6 mmol) was added to a cooled (−78 °C) solution of dianion **2a** (0.3 mmol)[7] in THF, and the stirred mixture was allowed to warm to room temperature for about 2 h. The color changed from yellow-brown to orange, and IR monitoring showed the formation of **3a**. IR (THF): $\tilde{\nu}(CO) = 2000$ (s), 1961 (vs), 1899 (s), 1876 (m), 1864 (m), 1829 cm^{-1} (w); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 47.8$ ppm; ^1H NMR (CD_2Cl_2): $\delta = 3.05$ (m, 3H; CH of *i*Pr, CH_2 of cod), 1.87 to 1.15 [m, 18H; CH_3 of *i*Pr).

4a: PEt_3 (40.7 μL, 0.3 mmol) was added to a solution of **3a** (0.3 mmol) in THF (prepared as described above), and the mixture was stirred at 40 °C for 1 h. The solvent was evaporated in vacuo, and the solid residue was dissolved in CH_2Cl_2/hexane (1:1) and filtered through alumina (activation degree III). Slow concentration of the filtrate gave **4a** (0.18 g, 82 %) as orange microcrystals with the correct C,H analysis. IR (THF): $\tilde{\nu}(CO) =$ 2002 (s), 1964 (s), 1899 (s), 1893 (sh), 1882 (m), 1651 cm^{-1} (w); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 48.4$ (s; SCP*i*Pr_3), −0.3 ppm (s, PEt_3); ^1H NMR (CD_2Cl_2): $\delta = 2.9$ (m, 3H; CH of *i*Pr), 1.94 (m, 6H; CH_2 of Et), 1.52 (m, 18H; CH_3 of *i*Pr), 1.05 ppm (m, 9H; CH_3 of Et).

5a: [$Pt(cod)Cl_2$] (0.118g, 0.3 mmol) was added to a cooled (−78 °C) solution of dianion **2a** (0.3 mmol)[7] in THF, and the stirred mixture was allowed to warm to room temperature while stirring for about 2 h. Workup as described for **4a** gave **5a** as orange microcrystals (0.15 g, 53 %) with correct C,H analysis. IR (THF): $\tilde{\nu}(CO) = 2002$ (s), 1971 (vs), 1902 (s), 1885 (sh), 1864 cm^{-1} (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 58.2$ ppm (s, $^3J(P,Pt) =$ 224.2); ^1H NMR (CD_2Cl_2): $\delta = 5.55$–5.22 (m, 4H; CH of cod), 2.97–2.14 (m, 11H; CH of *i*Pr, CH_2 of cod), 1.87 to 1.15 ppm (m, 18H; CH_3 of *i*Pr).

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[8] a) Crystal data for **4a**: $C_{22}H_{36}MnO_6PReS$, $M_r = 731.65$, crystal dimensions: 0.33 × 0.33 × 0.26, orthorhombic, space group $P2_12_12_1$, $a = 10.462(4)$, $b = 16.285(9)$, $c = 16.616(6)$ Å, $V = 2831(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.717\ g\,cm^{-3}$, $F(000) = 1448$; 2977 reflections with $1.75 < \theta <$ 25°. Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation ($\mu = 4.937\ mm^{-1}$), graphite monochromator. The structure was solved with DIRDIF,[8b] refinement with 2816 independent reflections ($R_{int} = 0.0317$) for 300 parameters against $|F^2|$ with SHELXTL[8c] gave $R = 0.0227$, $wR2 =$ 0.0619 (all data); max/min residual electron density 0.047/−0.471 e Å^3. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions; b) P. T. Beurskens, G. Admiraal, W. P. Bosman, G. Beurskens, H. M. Doesburg, S. García-Granda, R. O. Gould, J. M. M. Smits, C. Smikalla, *The DIRDIF Program System, Technical Report of the Crystallography Laboratory*, University of Nijmegen: The Netherlands, **1992**; c) G. M. Sheldrick, SHELXS-98, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany), **1998**.

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[10] Crystal data for **5a**: $C_{24}H_{33}MnO_6PPtReS_2 \cdot 0.5\,CH_2Cl_2$, $M_r = 988.26$, crystal dimensions: 0.40 × 0.20 × 0.13, monoclinic, space group $P2_1/n$, $a = 8.845(2)$, $b = 15.133(3)$, $c = 24.102(5)$ Å, $V = 3213(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.043\ g\,cm^{-3}$, $F(000) = 1872$; 6041 reflections with $1.59 < \theta <$ 25°. Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation ($\mu = 8.786\ mm^{-1}$), graphite monochromator. The structure was solved with DIRDIF,[8b] refinement with 5651 independent reflections ($R_{int} = 0.0452$) for 358 parameters against $|F^2|$ with SHELXTL[8c] gave $R = 0.0413$, $wR2 =$ 0.1322 (all data); max/min residual electron density 2.549 (at 0.91 Å from Pt)/−0.471 e Å^3. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions; b) CCDC-181580 and -181581 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[11] The Pt-Mn distance is shorter than 2.956(1) and 3.081 Å, which are found in the complex [{$(OC)_4Mn(\mu\text{-}PPh_2)\}_2Pt(PPh_3)$]: P. Braunstein, E. de Jesús, A. Dedieu, M. Lanfranchi, A. Tiripicchio, *Inorg. Chem.* **1992**, *31*, 399–410. The Mn-Re distance is very close to 2.830(1) Å found in the starting complex **1b**. B. Alvarez, D. Miguel, V. Riera, J. A. Miguel, S. García-Granda, *Organometallics* **1991**, *10*, 384–387.

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[13] The deprotonation[14] analogy can be used to consider the fragments {(cod)Pt} and {μ_3-S} isolobal with CH$_2$ and with CH$^-$. Since {Fe(CO)$_3$} is isolobal with CH$^+$, {Re(CO)$_3$} is isolobal with CH^{2+}. The thiocarbonylphosphorane can be split homolytically into S- and CPR$_3$, which is isolobal with CH. The planar ring can be considered as a (CH)$_5^+$ which is bonded through all five atoms to {Mn(CO)$_3$} (isolobal with CH^{2+}).

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Highly Enantioselective and Practical Cinchona-Derived Phase-Transfer Catalysts for the Synthesis of α-Amino Acids**

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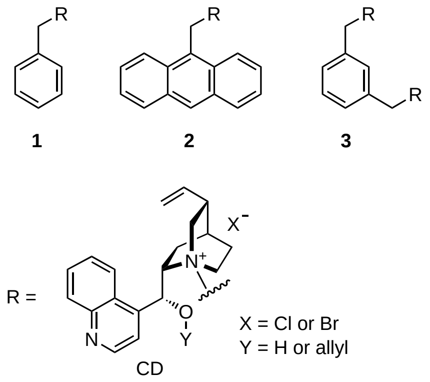
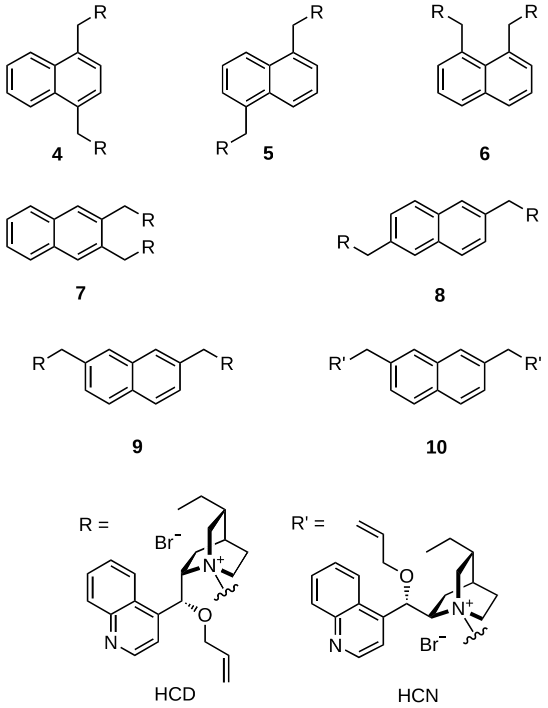
Phase-transfer catalysis (PTC) is one of the most useful methods for practical synthesis, because of its operational simplicity and mild reaction conditions, which enable this method to be applied to industrial processes.[1] Recently, PTC has been applied extensively to asymmetric synthesis by using chiral quaternary ammonium salts.[2] Chiral phase-transfer catalysts derived from the cinchona alkaloids have been developed and successfully applied to various useful organic reactions.[1d,e,3] Since the first cinchona alkaloid-type phase-transfer catalysts **1** were introduced by O'Donnell et al.,[4] more efficient catalysts **2** have been developed independently by Lygo et al.[5] and Corey et al.[6] by the introduction of the *N*-9-anthracenylmethyl group instead of the *N*-benzyl group in **1** (Scheme 1).



Scheme 1.

Based on the fact that the introduction of a bulky subunit at N1 of cinchona alkaloids leads to an enhancement of the stereoselectivity, we recently reported the efficient catalysts **3** by the formation of the *meta*-dimer, using benzene as a ligand (Scheme 1).[7] The enhancement of the stereoselectivity is a result of the screening effect between each cinchona unit (CD), which can make the substrate approach from only one direction. As part of our program to develop practical catalysts that can be used in industrial processes, we further investigated more optimal dimeric catalysts by modifying the ligand, that is, the benzene group in **3**. We report herein the preparation of new symmetrical dimeric cinchona-alkaloid-derived catalysts (Scheme 2), which have a naphthalene moiety as a ligand, and their application to the catalytic enantioselective phase-transfer alkylation of glycine derivative **11** (see Tables 1 and 2).



Scheme 2.

New dimeric quaternary ammonium salts **4**–**10** were prepared in two steps from (−)-hydrocinchonidine (for **4**–**9**) or (+)-hydrocinchonine (for **10**) and the corresponding bis(bromomethyl)naphthalenes, which can be easily prepared by the allylic bromination of the dimethylnaphthalenes. (−)-Hydrocinchonine or (+)-hydrocinchonine and the bis(bromomethyl)naphthalenes were stirred at 100 °C in EtOH/DMF/CHCl$_3$ (5:6:2) for 6 h, followed by O9-allylation with allyl bromide and aqueous KOH (50 %), to give the corresponding dimeric quaternary ammonium salts **4**–**10** in 90–95 % overall yields. The enantioselective efficiency of the naphthalene-based dimeric catalysts was evaluated by the enantioselective phase-transfer alkylation of **11**: the catalysts

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