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Synthesis, Molecular Structure and Reactions of a Novel μ-σ,π-Cyclopentadienediyl Platinum-Manganese Complex

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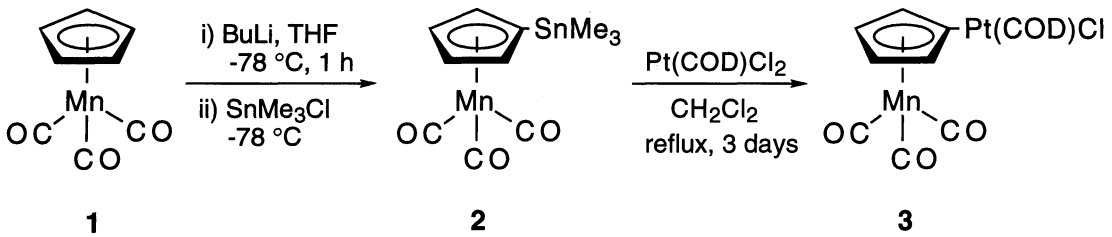
A novel σ,π-cyclopentadienediyl-bridged dinuclear complex {μ-η^1,η^5-C_5H_4Pt-(COD)Cl}Mn(CO)$_3$ (COD=1,5-cyclooctadiene) (**3**), of which structure was determined by X-ray crystallography, was prepared by the reaction between (η^5-$C_5H_4SnMe_3$)Mn-(CO)$_3$ and Pt(COD)Cl$_2$. The reaction of **3** with phosphine caused the ligand exchange reaction to give {μ-η^1,η^5-C_5H_4Pt(PR_3)Cl}Mn(CO)$_3$ (**4**). On treatment of complex **4b** (R=Et) with carbon monoxide acyl complex {η^5-C_5H_4COPt(PR_3)Cl}Mn(CO)$_3$ was obtained.

Multinuclear transition metal complexes in which hydrocarbon groups serve as bridging ligands are currently of great interest since they may give useful information on the active intermediate in the heterogeneous catalytic reactions.[1] Unsaturated hydrocarbon ligands have several bridging mode, for example there are three types, (σ,σ), (σ,π) and (π,π) for the dinuclear complexes.[1] A cyclopentadienyl ligand is one of the popular unsaturated hydrocarbon ligands in organometallic chemistry. Despite there have been prepared a lot of transition metal complexes possessing a σ,π-cyclopentadienediyl bridge, only a few complexes other than ferrocene derivatives have been reported.[2] In this communication we wish to describe the synthesis, molecular structure and reactions of a novel heterodinuclear μ-σ,π-cyclopentadienediyl complex of platinum-manganese.

For the synthesis of the μ-σ,π-cyclopentadienediyl complex, we applied the transmetallation from a trimethyltin compound to Pt(COD)Cl$_2$ (COD=1,5-cyclooctadiene).[3] Thus, treatment of (η^5-$C_5H_4SnMe_3$)Mn-(CO)$_3$ (**2**), which was prepared in 83% yield by the reaction of (η^5-C_5H_5)Mn(CO)$_3$ (**1**) with *n*-BuLi followed by the addition of Me_3SnCl, with Pt(COD)Cl$_2$ in dichloromethane under reflux afforded yellow crystals of {μ-η^1, η^5-C_5H_4Pt(COD)Cl}Mn(CO)$_3$ (**3**) in 73% yield.[4] Complex **3** was characterized by spectroscopic and crystallographic analyses,[5] and the molecular structure is presented in Fig. 1.



The Pt(1) atom is located at a distance of 3.667(2) Å from Mn(1), indicating that there is not any significant interaction between Pt and Mn. The bond length of Pt(1)-C(1) is 2.04(1) Å, which falls in the normal range of Pt-C(sp^2) single bond.[6] The Pt(1)-C(9) and Pt(1)-C(10) bond lengths [2.18(1) and 2.16(1) Å] are shorter than those of Pt(1)-C(13) and Pt(1)-C(14) [2.29(1) and 2.26(1) Å], and the bond distance of C(9)-C(10) [1.42(1) Å] is longer than that of C(13)-C(14) [1.35(1) Å].[7] These phenomena depend on the difference of *trans* influence between the chloride ligand and the cyclopentadiene-diyl ligand. The plane consisting of Pt(1), Cl(1) and C(1) is essentially parallel to the Cp ring and the dihedral angle is 4.4°.

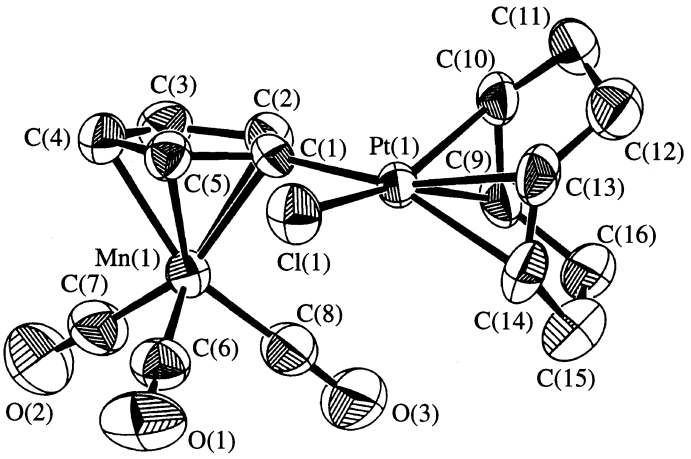
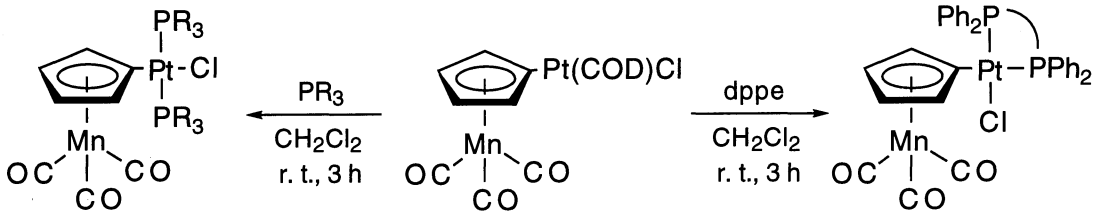


Fig. 1. ORTEP drawing of complex **3**; selected bond distances (Å) and bond angles (°): Pt(1)-Cl(1) 2.326(3), Pt(1)-C(1) 2.04(1), Pt(1)-C(9) 2.18(1), Pt(1)-C(10) 2.16(1), Pt(1)-C(13) 2.29(1), Pt(1)-C(14) 2.26(1), Mn(1)-C(1) 2.159(9), Mn(1)-C(2) 2.14(1), Mn(1)-C(3) 2.15(1), Mn(1)-C(4) 2.14(1), Mn(1)-C(5) 2.142(9), C(9)-C(10) 1.42(1), C(13)-C(14) 1.35(1); Cl(1)-Pt(1)-C(1) 91.1(3).

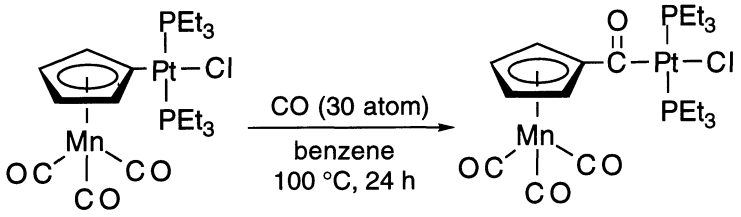


4a: R=Et
4b: R=Bu

3

4c

Treatment of **3** with triethylphosphine caused a ligand exchange reaction to give complex **4a** in 81% yield.[8] Similarly complex **3** was converted to complexes **4b** and **4c** in 73 and 85% yields, respectively.[9] The ^{31}P NMR spectra of these complexes exhibit that complexes **4a** and **4b** change into a *trans* configuration, while complex **4c** has a *cis* form.



4a

5

Then we have also investigated the reactivity of **4a** with carbon monoxide. Reaction of **4a** with CO (30 atom) at 100 °C gave complex **5** in 63% yield,[10] though any reaction was not observed at 50 °C. The appearance of a ν(CO) absorption at 1600 cm^{-1} as well as 1900 and 1911 cm^{-1} in the IR spectrum of **5** suggests that CO insertion have occurred to give an acyl complex, which was supported by means of ^{1}H, ^{13}C and ^{31}P NMR spectra. The molecular structure of **5** was determined by an X-ray diffraction analysis.[11]

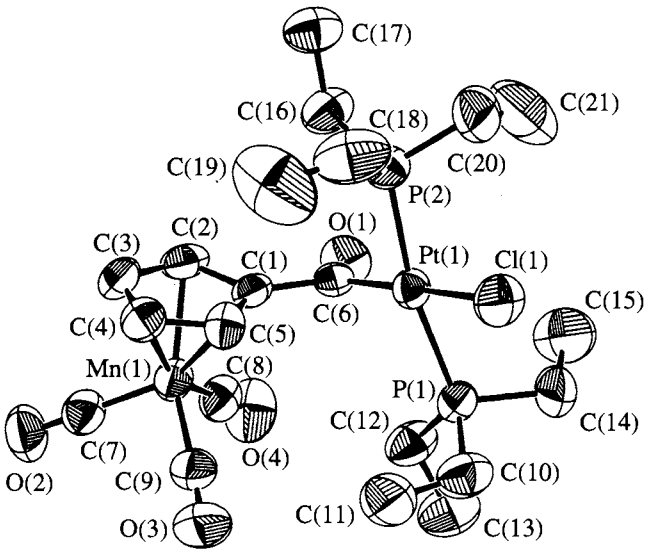


Fig. 2. ORTEP drawing of complex **5**; selected bond distances (Å) and bond angles (°): Pt(1)-Cl(1) 2.412(2), Pt(1)-P(1) 2.304(3), Pt(1)-P(2) 2.313(3), Pt(1)-C(6) 1.991(9), Mn(1)-C(1) 2.154(8), Mn(1)-C(2) 2.118(9), Mn(1)-C(3) 2.133(9), Mn(1)-C(4) 2.142(8), Mn(1)-C(5) 2.139(8), C(1)-C(6) 1.51(1); Cl(1)-Pt(1)-P(1) 87.44(9), Cl(1)-Pt(1)-P(2) 87.67(9), Cl(1)-Pt(1)-C(6) 177.1(3), P(1)-Pt(1)-P(2) 169.75(9), P(1)-Pt(1)-C(6) 93.7(2), P(2)-Pt(1)-C(6) 91.6(2).

As shown in Fig. 2, CO has inserted into the Pt-C bond of **4a** to produce **5**. Complex **5** has a slightly distorted square-planer geometry at the Pt atom with the triethylphosphine ligands in the *trans* position. The bond angle of ∠P(1)-Pt(1)-P(2) is 169.75(9)° and the P(1) and P(2) atoms are deviated from the least-square plane of Pt(1)Cl(1)P(1)P(2)-C(6) for 0.167(3) and 0.182(3) Å, respectively, which may depend on the steric repulsion with a $(C_5H_4)Mn(CO)_3$ moiety. The bond distance of Pt(1)-C(6) is 1.991(9) Å, which is typical for the acylplatinum complex.[12] The plane of acyl group Pt(1)C(6)O(1)C(1) is twisted from the Cp ring and the Pt coordination plane for 20.6° and 78,1°, respectively.

The reaction conditions in the carbonylation of **4a** are similar to that in the reaction of *trans*-$PtXPh(PR_3)_2$.[13] It was reported that migratory insertion of CO into the Pt-C bonds of $PtXR(CO)(PR'_3)$, which is an intermediate of the cabonyl-insertion reactions of *trans*-$PtXR(PR_3)_2$, is dramatically affected by the nature of the organic group bonded to the platinum; the tendency is as follows: Et>Ph>Me>>C_5H_5.[14] The strong electron donating properties of the π-bonded transition metal may enable the above carbonylation;[15] the details of the above interesting properties are currently under investigation.

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4) Spectroscopic data for **3**: ^{1}H NMR (399.65 MHz, C_6D_6), δ 5.36-5.34(m, 2H, =CH), 4.84(s, 2H, Cp), 4.29(s, 2H, Cp), 4.26-4.25(m, 2H, =CH), 1.72-1.58(m, 4H, CH_2), 1.33-1.24(m, 4H, CH_2); ^{13}C NMR (100.40 MHz, C_6D_6), δ 226.98(CO), 113.31(=CH), 98.93, 88.50(C_5H_4), 87.77(=CH), 83.47(C_5H_4), 31.06(CH_2), 27.86(CH_2).

5) Crystal data for **3**: $C_{16}H_{16}ClO_3MnPt$, M=541.78, space group *P2/n*, *a*=12.393(1) Å, *b*=7.128(1) Å, *c*=19.213(1) Å, *β*=105.405(6) °, *V*=1636.4(3) Å^3, *Z*=4, D_c=2.199 gcm^{-3}, *μ*=95.44 cm^{-1}, λ(Mo-K$_\alpha$)= 0.71069 Å, ω-2θ scan, $2\theta_{max}$=55.1°. The structure was solved by Patterson method and refined to R= 0.020 and R_W=0.027 for 199 parameters against 1523 (F>4σ(F)) out of 4087 unique reflections.

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8) Spectroscopic data for **4a**: ^{1}H NMR (399.65 MHz, C_6D_6), δ 4.26(t, J=1.7 Hz, 2H, Cp), 4.19(t, J=2.0 Hz, 2H, Cp), 1.79-1.72(m, 12H, CH_2), 0.93(dt, J=15.6, 7.8 Hz, 18H, CH_3); ^{13}C NMR (100.40 MHz, C_6D_6), δ 227.89(CO), 93.05, 92.66, 80.72(C_5H_4), 14.53(CH_2), 8.17(CH_3); ^{31}P NMR (161.70 MHz, C_6D_6), δ 19.30($^{1}J_{Pt\text{-}P}$=2673 Hz).

9) Spectroscopic data for **4b**: ^{1}H NMR (399.65 MHz, C_6D_6), δ 4.31(t, J=2.0 Hz, 2H, Cp), 4.25(t, J=1.7 Hz, 2H, Cp), 1.93-1.89(m, 12H, CH_2), 1.52-1.35(m, 24H, CH_2), 0.92(t, J=7.4 Hz, 18H, CH_3); ^{13}C NMR (100.40 MHz, C_6D_6), δ 227.90(CO), 94.12, 92.34, 80.77(C_5H_4), 26.57, 24.60, 22.23(CH_2), 14.04 (CH_3); ^{31}P NMR (161.70 MHz, C_6D_6), δ 11.39($^{1}J_{Pt\text{-}P}$=2655 Hz). For **4c**: ^{1}H NMR (399.65 MHz, C_6D_6), δ 7.89-7.84(m, 4H, Ph), 7.70-7.66(m, 4H, Ph), 7.04-6.96(m, 12H, Ph), 4.90(d, J= 1.5 Hz, 2H, Cp), 4.25(d, J=1.4 Hz, 2H, Cp), 1.84-1.71(m, 2H, CH_2), 1.57-1.45(m, 2H, CH_2); ^{31}P NMR (161.70 MHz, C_6D_6), δ 50.24($^{1}J_{Pt\text{-}P}$=1867 Hz), 47.89($^{1}J_{Pt\text{-}P}$=3982 Hz).

10) Spectroscopic data for **5**: ^{1}H NMR (399.65 MHz, C_6D_6), δ 5.16(t, J=2.2 Hz, 2H, Cp), 3.89(t, J=2.2 Hz, 2H, Cp), 1.80-1.66(m, 12H, CH_2), 1.00(dt, J=16.6, 7.8 Hz, 18H, CH_3); ^{13}C NMR (100.40 MHz, C_6D_6), δ 224.73(MnCO), 206.57 (PtCO), 111.69, 86.06, 81.17(C_5H_4), 14.68(CH_2), 8.00(CH_3); ^{31}P NMR (161.70 MHz, C_6D_6), δ 19.81($^{1}J_{Pt\text{-}P}$=2957 Hz).

11) Crystal data for **5**: $C_{21}H_{34}ClO_4P_2MnPt$, M=697.93, space group $P2_1/a$, *a*=13.612(3) Å, *b*=11.031(2) Å, *c*=18.381(2) Å, *β*=103.79(1) °, *V*=2680.4(8) Å^3, *Z*=4, D_c=1.729 gcm^{-3}, *μ*=59.61 cm^{-1}, λ(Mo-K$_\alpha$)= 0.71069 Å, ω-2θ scan, $2\theta_{max}$=55.1°. The structure was solved by Patterson method and refined to R= 0.028 and R_W=0.023 for 271 parameters against 2267 (I>5σ(I)) out of 6516 unique reflections.

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