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The Molecular Structure of the Heterodinuclear Organometallic Complex of Platinum and Tungsten, Phenyl(1,5-cyclooctadiene)platinum-tricarbonyl(η^5-cyclopentadienyl)tungsten

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Synopsis. The structure of the novel heterodinuclear organometallic complex, [(cod)(Ph)Pt-W(CO)$_3$(η^5-C$_5$H$_5$)] has been determined by X-ray crystallography; the Pt-W bond distance is 2.844(1)Å.

Special attention has been drawn recently to heterobimetallic compounds from the viewpoint of their catalytic abilities.1) Little is so far known, however, about chemistry of heterodinuclear organometallic complexes, especially those containing a direct bond between different transition metals.2) We have recently reported the preparation of a series of heterodinuclear organometallic complexes containing platinum and tungsten of the type, [(cod)(R)Pt-W(CO)$_3$(η^5-C$_5$H$_5$)] (R=Me, Et, Ph, or tolyl), which show a unique alkyl-transfer reaction from the platinum to tungsten atoms.3) We describe here the structure of one of these complexes, [(cod)(Ph)Pt-W(CO)$_3$(η^5-C$_5$H$_5$)] established by X-ray crystallography.

Experimental

The title compound was prepared by the method previously reported.3) The crystals were obtained as deep red plates from dichloromethane-hexane solutions.

Crystal Data. $C_{22}H_{22}O_3PtW$, M=713.4, monoclinic, $P2_1/n$, a=14.291(3), b=12.731(2), c=12.027(3), Å, β=112.48(2)°, U=2021.9(7) Å^3, Z=4, D_c=2.343 g cm^{-3}, μ(Mo $K\alpha$)=133.1 cm^{-1}.

A crystal with approximate dimensions of 0.10×0.50×0.55 mm sealed in a thin-glass capillary under nitrogen was mounted on a Rigaku automated four-circle diffractometer. Accurate unit-cell parameters were determined by the least-squares fit of 2θ values of 25 strong reflections (21.8<2θ<29.9°). Intensity data collection was carried out using Mo$K\alpha$ radiation by the θ-2θ scan mode. The scan speed and range were 4° min^{-1} in 2θ and $\Delta(2\theta)=(1.8+0.7\tan\theta)°$, respectively. The background intensities were measured for 5 s at both ends of a scan. A total of 4413 independent reflections (R_{int}=0.012) were collected with $\sin\theta/\lambda$ up to 0.64. Absorption correction was applied to the intensity data.4) The minimum normalized transmission factor which was based on intensities obtained by the azimuthal scan of 404 and $\bar{4}0\bar{4}$ reflections was 0.10.

The structure was solved by the heavy atom method and refined by the block-diagonal least-squares procedure using HBLS-V.5) Non-hydrogen atoms were refined anisotropically except for the C(1), C(20), and O(1) atoms which were refined with the isotropic thermal parameters. All the hydrogen atoms whose positions were estimated from stereochemical consideration were included in the structure factor calculation. At the final stages of refinement, two reflections (200 and 002) were excluded due to the extinction effects. The final R and R_w values are 0.070 and 0.075 for 3778 [$|F_o|>3\sigma(|F_o|)$] reflections. The weighting scheme used in the final refinement cycles is $w=(\sigma_{cs}^2-0.100|F_o|+0.017|F_o|^2)^{-1}$. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.6) The final atomic parameters are listed in Table 1.§

Table 1. Fractional Atomic Coordinates and (Equivalent) Isotropic Thermal Parameters of Non-H Atoms with e.s.d.'s in Parentheses

Atom	x	y	z	B_{eq} a)/B**(Å^2)
Pt	0.39951(3)	0.27668(3)	0.27760(4)	2.8
W	0.54984(4)	0.36778(3)	0.20679(4)	3.2
C(1)	0.4527(9)	0.1388(7)	0.2442(11)	3.4(2)**
C(2)	0.5298(9)	0.0870(8)	0.3332(11)	3.8
C(3)	0.5644(11)	−0.0127(8)	0.3077(15)	5.8
C(4)	0.5229(12)	−0.0611(8)	0.2018(16)	6.0
C(5)	0.4386(12)	−0.0079(9)	0.1084(13)	5.4
C(6)	0.4044(9)	0.0907(8)	0.1308(12)	4.1
C(7)	0.2605(9)	0.2010(7)	0.2812(12)	4.1
C(8)	0.3399(9)	0.1957(7)	0.3969(11)	3.7
C(9)	0.3500(11)	0.2640(8)	0.5008(12)	4.7
C(10)	0.3232(10)	0.3822(8)	0.4725(12)	4.3
C(11)	0.3539(9)	0.4209(7)	0.3725(11)	4.1
C(12)	0.2941(10)	0.4253(7)	0.2522(11)	3.9
C(13)	0.1900(10)	0.3806(8)	0.1955(12)	4.7
C(14)	0.1704(9)	0.2797(8)	0.2469(13)	4.5
C(15)	0.6950(12)	0.2772(13)	0.2503(15)	7.9
C(16)	0.7131(14)	0.3843(11)	0.2099(20)	8.9
C(17)	0.6488(14)	0.3911(11)	0.0949(20)	8.5
C(18)	0.5982(15)	0.2994(13)	0.0602(16)	8.6
C(19)	0.6264(11)	0.2280(9)	0.1456(15)	5.7
C(20)	0.5292(10)	0.5176(8)	0.2159(11)	4.1(3)**
C(21)	0.5694(9)	0.3534(6)	0.3781(10)	3.5
C(22)	0.4075(9)	0.3577(7)	0.0932(11)	3.8
O(1)	0.5192(8)	0.6081(6)	0.2247(9)	5.7(2)**
O(2)	0.5957(7)	0.3482(6)	0.4832(8)	4.9
O(3)	0.3303(7)	0.3575(6)	0.0117(9)	5.7

a) As defined by Hamilton.7)

Computations were done on an ACOS 930 computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University.

Results and Discussion

The molecular structure is depicted in Fig. 1 with atomic numbering systems. Bond distances and angles are listed in Table 2. The Pt-W bond distance is 2.844(1) Å, which is corresponding to the sum of

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§ Tables for anisotropic temperature factors, for atomic coordinates of hydrogen atoms, and for observed and calculated structure factors are deposited as Document No. 8909 at the Office of the Editor of Bull. Chem. Soc. Jpn.

covalent bond radii of platinum and tungsten [2.85 Å]. This value falls in the range of metal-to-metal bond lengths [2.60—2.90 Å average 2.76 Å] in the platinum-tungsten complexes so far reported[9] but is classified to somewhat long distance among them.

The geometry around the platinum atom is typically square-planar where the carbon (phenyl) atom, the centers of two C=C double bonds of the cod ligand, and the tungsten atom are coplanar to each other [maximum deviation 0.07 Å]. It is noteworthy that the tungsten atom occupies one of four corners of the square-planar geometry, because platinum-tungsten complexes whose structures have been hitherto elucidated[9] always contain bridging μ-ligands between two metal atoms and the arrangement of ligands around the platinum atom is far from square-planer geometry.[§§] On the other hand, the geometry around the tungsten atom is square-pyramidal, where the center of the η^5-C_5H_5 ligand is located at an apical position. These geometrical features around both metal atoms are consistent with the d^8 and d^6 electronic configurations of platinum and tungsten, respectively, which are also supported by the spectroscopic results.[3]

Table 2. Selected Bond Distances and Bond Angles for Non-H Atoms with e.s.d.'s in Parentheses

(a) Bond distance/Å			
Pt-W	2.8435(7)	Pt-C(1)	2.014(13)
Pt-C(7)	2.223(14)	Pt-C(8)	2.186(13)
Pt-C(11)	2.381(13)	Pt-C(12)	2.365(14)
Pt-C(21)	2.463(12)	Pt-C(22)	2.488(13)
W-C(15)	2.254(18)	W-C(16)	2.328(24)
W-C(17)	2.314(24)	W-C(18)	2.297(21)
W-C(19)	2.350(18)	W-C(20)	1.940(14)
W-C(21)	1.979(12)	W-C(22)	1.974(13)
C(1)-C(2)	1.38(2)	C(1)-C(6)	1.41(2)
C(2)-C(3)	1.44(3)	C(3)-C(4)	1.33(3)
C(4)-C(5)	1.46(3)	C(5)-C(6)	1.41(3)
C(7)-C(8)	1.42(2)	C(7)-C(14)	1.56(2)
C(8)-C(9)	1.48(2)	C(9)-C(10)	1.56(2)
C(10)-C(11)	1.51(2)	C(11)-C(12)	1.37(2)
C(12)-C(13)	1.49(2)	C(13)-C(14)	1.50(2)
C(15)-C(16)	1.50(3)	C(15)-C(19)	1.41(3)
C(16)-C(17)	1.34(4)	C(17)-C(18)	1.35(4)
C(18)-C(19)	1.31(3)	C(20)-O(1)	1.17(2)
C(21)-O(2)	1.17(2)	C(22)-O(3)	1.16(2)

(b) Bond angle/°			
W-Pt-C(1)	84.8(4)	W-Pt-C(7)	164.9(4)
W-Pt-C(8)	156.5(4)	W-Pt-C(11)	101.9(4)
W-Pt-C(12)	98.8(4)	W-Pt-C(21)	43.1(3)
W-Pt-C(22)	42.8(3)	C(1)-Pt-C(7)	92.0(5)
C(1)-Pt-C(8)	89.5(5)	C(1)-Pt-C(11)	164.1(5)
C(1)-Pt-C(12)	160.4(5)	C(7)-Pt-C(11)	85.1(5)
C(7)-Pt-C(12)	79.6(5)	C(8)-Pt-C(11)	78.6(5)
C(8)-Pt-C(12)	94.2(5)		
Pt-W-C(15)	117.1(5)	Pt-W-C(16)	154.0(6)
Pt-W-C(17)	157.9(6)	Pt-W-C(18)	124.0(6)
Pt-W-C(19)	106.3(5)	Pt-W-C(20)	103.6(4)
Pt-W-C(21)	58.2(4)	Pt-W-C(22)	58.9(4)
C(16)-W-C(20)	94.8(8)	C(16)-W-C(21)	104.5(7)
C(16)-W-C(22)	141.1(7)	C(19)-W-C(20)	149.5(6)
C(19)-W-C(21)	111.0(6)	C(19)-W-C(22)	102.4(6)
C(20)-W-C(21)	89.8(6)	C(20)-W-C(22)	87.9(6)
C(21)-W-C(22)	114.4(6)		
Pt-C(1)-C(2)	120.9(10)	Pt-C(1)-C(6)	119.2(10)
Pt-C(7)-C(8)	69.8(8)	Pt-C(7)-C(14)	111.8(9)
C(8)-C(7)-C(14)	124.0(12)	Pt-C(8)-C(7)	72.6(8)
Pt-C(8)-C(9)	109.8(9)	C(7)-C(8)-C(9)	125.5(12)
C(8)-C(9)-C(10)	116.5(12)	C(9)-C(10)-C(11)	111.6(12)
Pt-C(11)-C(10)	110.2(9)	Pt-C(11)-C(12)	72.6(8)
C(10)-C(11)-C(12)	126.8(12)	Pt-C(12)-C(11)	73.9(8)
Pt-C(12)-C(13)	103.2(9)	C(11)-C(12)-C(13)	125.3(12)
C(12)-C(13)-C(14)	116.7(12)	C(7)-C(14)-C(13)	113.2(12)
W-C(20)-O(1)	178.0(12)	W-C(21)-O(2)	170.1(11)
W-C(22)-O(3)	168.1(12)		

The other remarkable features of the structure are the existences of strong trans-influence on the platinum atom and of the weak interaction between the platinum atom and two CO groups. Firstly, the Pt-C(11) and Pt-C(12) bonds (trans to C(phenyl)) of 2.381(13) and 2.365(14) Å are obviously longer than the Pt-C(7) and Pt-C(8) bonds (trans to W) of 2.223(14) and 2.186(13) Å. This shows stronger trans-influence from the phenyl group than that from the tungsten atom. Secondly, among three carbonyl groups attached to the tungsten atom, two of them (C(21)≡O(2) and C(22)≡O(3)) are located as if attacking the Pt-W bond from both sides. Although the Pt···C(21) and Pt···C(22) distances of 2.463(12) and 2.488(12) Å are much longer than those expected for the Pt-C bond as the μ-CO ligands, the W-C(21) and

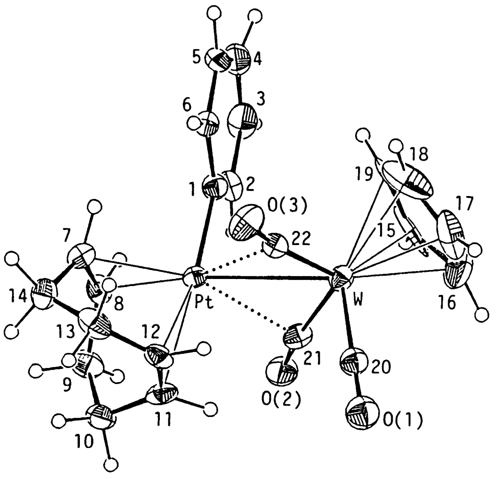

Fig. 1. The molecular structure[8] of [(cod)(Ph)Pt-W(CO)$_3$(η^5-C_5H_5)] together with the numbering scheme (only atomic numbers are shown for carbon atoms). Non-hydrogen atoms are represented by thermal ellipsoids at 30% probability levels, while hydrogen atoms are drawn by spheres with B=1.0 Å^2. Selected coordination angles not appeared in Table 2 are as follows; W-Pt-C(11/12)=100.8, C(1)-Pt-C(7/8)=90.8, C(7/8)-Pt-C(11/12)=83.8 (C(7/8) and C(11/12): midpoints of the C(7)-C(8) and C(11)-C(12) bonds, respectively), CCP-W-Pt=136.5, CCP-W-C(20)=119.9, CCP-W-C(21)=119.4, CCP-W-C(22)=117.9° (CCP: center of gravity of the η^5-cyclopentadienyl ring).

[§§] In the hydrido-bridged complex, [$(Et_3P)_2$(Ph)Pt(μ-H)W(H)(η^5-C_5H_5)$_2$], the square-planar geometry is apparently observed in case that the bridging hydrido ligand is ignored.[10]

W-C(22) bonds of 1.979(12) and 1.974(13) Å are slightly lengthened and the W-C(21)-O(2) and W-C(22)-O(3) angles of 170.1(11) and 168.1(12)° are slightly bent when compared with those of the other free CO group; W-C(20)=1.940(14) Å and W-C(20)-O(1)=178.0(12)°. These facts simply weak interaction of two CO groups to the platinum atom in spite of the fact that they hardly function as bridging μ-ligands.

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