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Oxidative Addition of the Mo–Cl Bond to the Pt_0 Complex. Synthesis and Structure of $Cp'Mo(\mu\text{-}CO)_2(C_2Ph_2)Pt_2(PPh_3)_2(CO)Cl$

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Abstract—A reaction of $Cp'Mo(CO)_3Cl$ ($Cp' = MeC_5H_4$) with $(PPh_3)_2Pt(C_2Ph_2)$ gave the heterometallic cluster $Cp'Mo(\mu\text{-}CO)_2(C_2Ph_2)Pt_2(PPh_3)_2(CO)Cl$ (I) as the sole product. According to X-ray diffraction data, complex I contains single Pt–Mo bonds (2.7962(5) and 2.7699(5) Å) but no Pt–Pt bond (Pt⋯Pt 2.9746(3) Å). The coordinated diphenylacetylene molecule forms two Pt–C σ-bonds (2.054(6) and 2.083(5) Å) and a π-bond to the Mo atom (Mo–C 2.265(6) and 2.272(5) Å; C≡C 1.387(8) Å).

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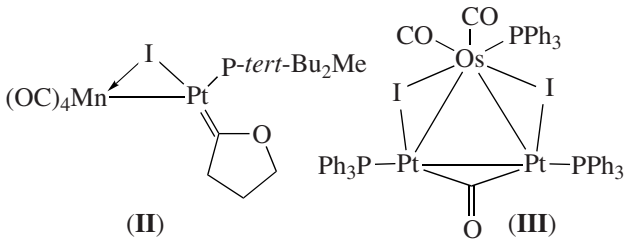
Bimetallic catalysts containing platinum or palladium are widely used in the production of important organic products [1]. Heterometallic clusters can serve as precursors of active and selective bimetallic nanosized catalysts, e.g., for hydrogenation reactions when applied to appropriate oxide substrates [2]. Their specific properties are due to the synergetic effect of two dissimilar metals [3].

A common route to heterometallic platinum-containing clusters with direct metal–metal bonds involves replacement of a halogen atom at Pt under the action of various carbonylmetalate anions $CpM(CO)_3^-$ (M = Cr, Mo, and W) [4–6], $Mn(CO)_5^-$ [4], $Co(CO)_4^-$ [7], and $Fe(CO)_3NO^-$ [8]. Alternatively, the target clusters can be obtained by addition of Pt_0 complexes to metal–metal bonds [9] or by insertion of them into metal–hydrogen [10] or chalcogen–chalcogen bonds in a complex of a different transition metal [11, 12]. Oxidative addition of compounds containing a Sn–Cl [13] or Hg–Cl bond [14] also yields heterometallic complexes. At the same time, a reaction of $Pt(P\text{-}tert\text{-}Bu_2Me)(C_2H_4)_2$ with the manganese carbene complex $MnI(COCH_2CH_2CH_2)(CO)_4$ involves transfer of the carbene ligand to platinum and coordination of the Pt atom to the resulting formally double Mn=I bond (by analogy with olefin coordination) to give the heterobinuclear complex $MnPt(\mu\text{-}I)(COCH_2CH_2CH_2)(CO)_4(P\text{-}tert\text{-}Bu_2Me)$ (**II**) [15]. On the other hand, treatment of $Os_2(CO)_6(\mu\text{-}I)_2$ with $(PPh_3)_2Pt(C_2Ph_2)$ results in transmetalation with ligand exchange, addition of two platinum-containing fragments to the Os–I bonds, and the formation of the cluster $OsPt_2(\mu\text{-}CO)(\mu\text{-}I)_2(CO)_2(PPh_3)_3$ (**III**) [16]:



We found it interesting to study a reaction of a Pt_0 complex with $Cp'Mo(CO)_3Cl$ under heating.

EXPERIMENTAL

All manipulations dealing with the synthesis and isolation of the products were carried out under argon in dehydrated solvents. The complex $(PPh_3)_2Pt(C_2Ph_2)$ was prepared as described in [17]; $Cp'Mo(CO)_3Cl$ (**IV**) was prepared by analogy with the synthesis of $CpMo(CO)_3Cl$ [18]. The IR spectrum of complex **IV** in the range of CO stretches (2045 s, 1975 s, 1950 vs; in CH_2Cl_2) agrees with literature data [19]. IR spectra were recorded on a Specord 75IR spectrophotometer (KBr pellets). Elemental analysis was performed on a CHNS analyzer (Carlo Erba) at the Institute of General and Inorganic Chemistry of the Russian Academy of Sciences.

Synthesis of $Cp'Mo(CO)_2(C_2Ph_2)Pt_2(PPh_3)_2(CO)Cl$ (I). A solution of complex **IV** (0.1 g, 0.34 mmol) and $(PPh_3)_2Pt(Ph_2C_2)$ (0.6 g, 0.67 mmol) in THF (60 ml) was refluxed for 2 h. The solvent was removed *in vacuo*. An oily residue was washed with light petroleum (2 × 10 ml) and diethyl ether (10 ml). The washing resulted in partial dissolution of the residue and in crystallization of the undissolved product. The crystalline residue was dissolved almost completely in CH_2Cl_2 (20 ml), the solution was filtered, and hexane (8 ml) was added to the mother liquor. The mixture was concentrated *in vacuo* to half its volume and kept at –10°C for a day. The red-orange crystals that formed were separated by decanting, washed with hexane (10 ml), and dried *in vacuo*. The yield of the solvate $\mathbf{I} \cdot CH_2Cl_2$ was 0.124 g (25%).

Found (%):	C 49.10;	H 2.98.
For $C_{59}H_{47}O_3P_2ClMoPt_2 \cdot CH_2Cl_2$		
anal. calcd. (%):	C 48.94;	H 3.35.

IR (ν, cm^{-1}): 2015 vs, 1910 m, 1710 s (*ν*(CO)), 1470 w, 1420 m, 1080 m, 730 w, 680 vs, 585 w, 510 vs.

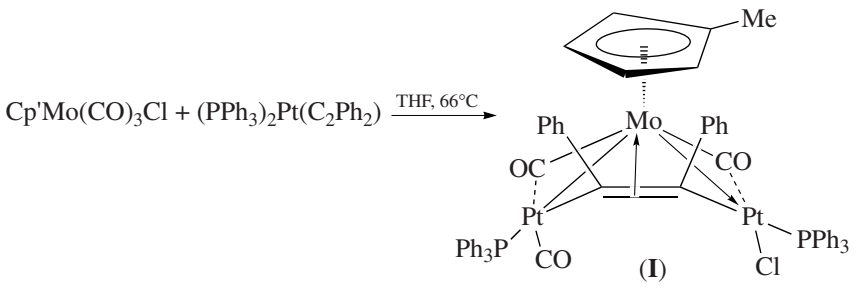
The crystals of the solvate $I \cdot 1.5CH_2Cl_2$ suitable for X-ray diffraction analysis were obtained by crystallization at the CH_2Cl_2–hexane interface.

X-ray diffraction analysis. Crystallographic parameters and a summary of data collection and refinement for $I \cdot nCH_2Cl_2$ are given in Table 1. The structure was solved by the direct method and refined by the least-squares method on F^2 in the anisotropic approximation for the non-hydrogen atoms with the SHELXTL program package [20]. In the crystal, the solvate CH_2Cl_2 molecule is disordered over two positions with difficult-to-refine populations. Since the solvate molecules are beyond the scope of this study and do not influence the geometry of the cluster under discussion, we refined structure **I** proper (with no regard to solvate CH_2Cl_2 molecules) with the "squeeze" technique of the PLATON program package [21]. We excluded from our consideration a space with a volume of 395 Å^3 and 66 electrons, which corresponds to 1.5 molecules of CH_2Cl_2 per structure **I** (its presence was confirmed by elemental analysis data for complex **I**). Using the PLATON/SQUEEZE procedure, we reduced by half the discrepancy factor R_1 (for reflections with $I > 2\sigma(I)$); the final residual was $R = 0.0389$. Selected bond lengths and angles in structure I are given in Table 2. The hydrogen atoms were located geometrically.

Atomic coordinates and other structural parameters of complex **I** have been deposited with the Cambridge Crystallographic Data Collection (no. 710243); see http://www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

A reaction of complex **IV** with $(PPh_3)_2Pt(C_2Ph_2)$ in boiling THF gives complex **I** as the sole product detected by TLC and IR spectroscopy. No other products were obtained, regardless of the ratio of the reagents. Complex $\mathbf{I} \cdot 1.5CH_2Cl_2$ was isolated as orange-red crystals that are stable in air. According to X-ray diffraction data (figure), either Pt atom in structure **I** is in a distorted square environment. The single Mo–Pt bonds (2.7962(5) and 2.7699(5) Å) in the angular $MoPt_2$ framework are similar to those found in the known cluster $[Pt_2Mo(\mu\text{-}CO)_3(\mu\text{-}PPh_2)Cp(PPh_3)_2]$ (**V**) (Pt–Mo 2.796 and 2.814 Å) [6]. The framework of complex **I** comprises two more electrons and the Pt···Pt distance is nonbonding (2.9746(3) Å), as distinct from the bonding distance in structure **V** (2.605 Å).



Note that two identical Pt–Mo bonds (2.777(2) and 2.793(1) Å) make up a planar framework Pt_2Mo_2 in $Cp_2Mo_2Pt_2(CO)_6(PEt_3)_2$ [4], although the second pair of the Pt–Mo bonds are longer (2.835(2) and 2.846(1)Å) as in complexes with linear frameworks $([(Me_2NC_5H_4)Mo(CO)_3]_2PtL_2$, where L is MeCN or

Table 1. Crystallographic parameters and a summary of data collection and refinement for structure **I**

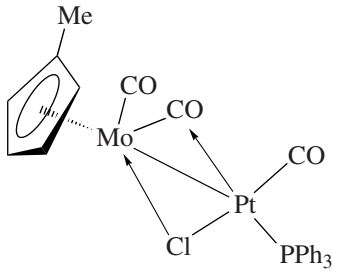
Parameter	Value
Diffractometer	Bruker APEX II CCD
M	1387.48
Radiation (λ, Å)	MoK_α (0.71073)
Temperature, K	296(2)
Space group	$C2/c$
a, Å	25.4342(11)
b, Å	11.3706(5)
c, Å	39.2098(16)
β, deg	91.4190(10)
V, Å^3	11336.1(8)
Z	8
ρ(calcd), g/cm^{-3}	1.626
μ, mm^{-1}	5.286
F(000)	5360
θ scan range, deg	1.04–26.00
Scan mode	ω
Number of independent reflections (N_1)	11120 (R_{int} = 0.0214)
Number of reflections with $I > 2\sigma(I)$ (N_2)	9628
Number of parameters refined	614
GOOF (F^2)	1.113
R_1 for N_2	0.0389
wR_2 for N_1	0.0928
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.719/–1.956

Table 2. Selected bond lengths and angles in structure **I**

Bond	d, Å	Bond	d, Å
Pt(1)–Mo(1)	2.7962(5)	C(4)–C(3)	1.387(8)
Pt(2)–Mo(1)	2.7699(5)	Mo(1)–C(1)	1.968(7)
Pt(1)–Pt(2)	2.9746(3)	Mo(1)–C(2)	2.025(6)
Pt(1)–P(1)	2.3112(14)	Pt(1)–C(1)	2.592(7)
Pt(2)–P(2)	2.3536(16)	Pt(2)–C(2)	2.075(6)
Pt(2)–Cl(1)	2.3697(15)	Angle	ω, deg
Mo(1)–C(4)	2.265(6)	C(4)C(3)C(11)	130.7(6)
Mo(1)–C(3)	2.272(5)	C(3)C(4)C(5)	131.0(5)
Pt(1)–C(3)	2.054(6)	O(2)C(2)Mo(1)	146.6(5)
Pt(2)–C(4)	2.083(5)	O(1)C(1)Mo(1)	163.7(5)

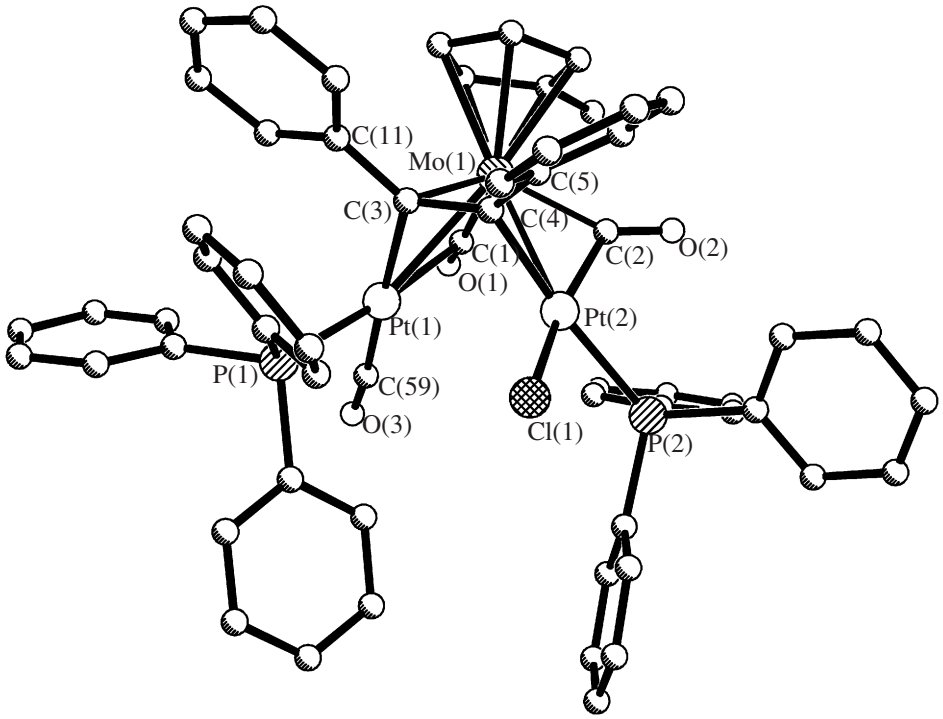
PhCN; Pt–Mo 2.868(1) and 2.854(3) Å [22]). Interestingly, the Pt–Mo distances remain virtually unchanged (2.7456(3) and 2.8466(3) Å) in $Cp_2Mo_2Pt_2(CO)_4$(P-*tert*-$Bu_3)_2$ [9] containing two less carbonyl ligands: the electron deficiency affects only the formation of the multiple Mo–Mo bond (2.6535(4) Å).

Apparently, in the synthesis of complex **I**, the first step involves coordination of the Pt_0 complex to the double Mo=Cl bond resulting from the detachment of a CO group from the starting complex **IV** (by analogy with the aforementioned reaction of (tetracarbonyl)(iodide)manganese [15]):



The second step involves addition of a second platinum-containing fragment, probably $(PPh_3)Pt(C_2Ph_2)$. The acetylene ligand donates four electrons to form two σ-bonds to the Pt atoms (Pt–C 2.054(6) and 2.083(5) Å) and a π-bond to the Mo atom (Mo–C 2.265(6) and 2.272(5) Å). This lengthens the acetylene C≡C bond to 1.387(8) Å and diminishes the CCC(Ph) angles to 131.0(5)° and 130.7(6)°. A similar structure of the coordinated acetylene has been found in the known clusters $MPt(CO)_5(PPh_3)_2(Ph_2C_2)$ (M = Fe, Ru, and Os) obtained from $(PPh_3)_2Pt(C_2Ph_2)$ and carbonyls of appropriate metals [23] and in the cluster $OsPt_2(CO)_5(PPh_3)_2(Me_2C_2)$ obtained from but-2-yne and the osmium platinum cluster $Os_3Pt(\mu\text{-}H)_2(CO)(PPh_3)$ [24].

The bridging CO ligands in cluster **I** are substantially different. The group with phosphine in the *trans*-position relative to the Pt–C bond is only partially (asymmetrically) bridging (Mo(1)–C(1) 1.968(7) Å, Pt(1)–C(1) 2.592(7) Å, the angle O(1)C(1)Mo(1) 163.7(5)°, ν(CO) 1910 cm^{-1}). The bridging CO ligand with the Cl atom in the *trans*-position relative to the Pt–C bond is virtually symmetrical (Mo(1)–C(2)



Molecular structure **I**.

2.025(6) Å, Pt(2)–C(2) 2.075(6) Å, the angle O(2)C(2)Mo(1) 146.6(5)°, ν(CO) 1710 cm^{-1}).

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