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Alkyl Transfer in the Heterodinuclear Organometallic Complex. Preparation of Organo(1,5-cyclooctadiene)platinum-tricarbonyl(cyclopentadienyl)tungsten

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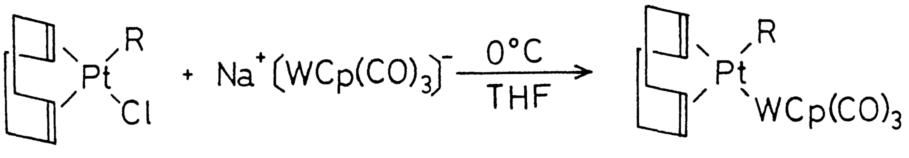
Methyl(1,5-cyclooctadiene)platinum-tricarbonyl(cyclopentadienyl)tungsten has been prepared by the reaction of methylchloro(1,5-cyclooctadiene)platinum(II) with sodium tricarbonyl(cyclopentadienyl)tungstate(0). Methyl transfer from platinum to tungsten smoothly takes place on thermolysis as well as by the reaction with tertiary phosphine ligands, CO, or olefins.

Chemical behavior of heterobimetallic compounds is a topic of considerable current interest in catalysis.1) In contrast to the extensive investigations on the mononuclear organometallic compounds, the chemistry of organic derivatives of heterobimetallic compounds, especially the complexes having a bond between two different transition metals, are much less explored so far.2) We now report the preparation of a series of heterodinuclear organometallic complexes involving platinum and tungsten, and their unique alkyl transfer from platinum to tungsten atoms.

The reaction of methylchloro(1,5-cyclooctadiene)platinum(II)3) with a stoichiometric amount of sodium tricarbonyl(cyclopentadienyl)tungstate(0)4) in THF at 0 °C slowly afforded a deep red solution in a few hours. After evaporating all volatiles, the residual dark red solid was extracted with benzene. The benzene extracts were recrystallized from dichloromethane-hexane to give deep red crystals, which were characterized as methyl(1,5-cyclooctadiene)platinum-tricarbonyl(cyclopentadienyl)tungsten, **1** by elemental analysis,5) NMR and IR spectra together with its chemical reactivity. Analogous derivertives containing ethyl, phenyl and o-tolyl groups, 2-4 were also prepared. These complexes are fairly air and thermally stable.



R=Me(1), Et(2), Ph(3), tolyl(4)

The ^{1}H NMR data of the complexes 1-4 are summarized in Table 1. A signal due to the methyl group attached directly to the platinum atom in 1 appears as a singlet with a ^{195}Pt satellites. Two kinds of signals, which also have ^{195}Pt satellites, assignable to olefinic protons of the cyclooctadiene ligand are observed, suggesting substantial difference of the trans influence of methyl from that of the tungsten moiety in the square planar platinum complex. Similar signals are also obtained for 2 and 3. However, both olefinic proton signals for 4 splitted further into two groups. This results suggest that the rotation of the o-tolyl ligand in 4 is restricted because of large steric bulkiness of the tungsten moiety. This ristricted rotation may give rise to different magnetic circumstances for these protons. A similar splitting is also observed in the methylene proton signals of the cyclooctadiene ligand. Cyclopentadienyl proton signals for 1-4 were observed as singlets. IR spectra of these complexes show strong ν(C=O) bands at ca. 1800 and 1900 cm^{-1}. The values are considerably lower than that of the neutral tricarbonyl(cyclopentadienyl)methyltungsten(II), but are quite similar to reported ν(C=O) values of the known tricarbonyl(cyclopentadienyl)tungstate anion. This fact suggests the strong back bonding of the tungsten moiety to the carbonyl ligands.5) From these spectroscopic results, the formal oxidation states of the platinum and the tungsten atoms in 1-4 are considered to be close to two and zero, respectively. A square planar structure around the platinum metal is consistent with a d^8 electronic configuration.

Acidolysis of 1 with sulfuric acid liberated a quantitative yield of methane (97% / 1), supporting the chemical formula of 1. Iodolysis of 1 in benzene induced cleavage of platinum-tungsten bond to give diiodo(1,5-cyclooctadiene)-platinum(II)6) and tricarbonyl(cyclopentadienyl)iodotungsten(II). In the course

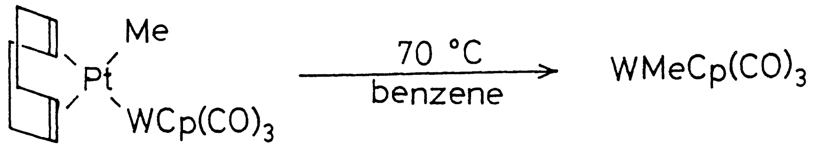
Table 1. Selected ^{1}H NMR Spectral Data of (CO)$_3$CpW-PtR(cod) in C$_6$D$_6$$^{a)}$

R	Pt-R	Cp	=CH- (cod)
Me	1.21s(75.4)	4.92s	5.2br(38), 4.4br(59)
Et	1.14t(48.6),1.98q(86.3)$^{b)}$	4.97s	5.5br(33), 4.4br(65)
Ph	7.4m(51.3), 7.0m, 6.7m	4.59s	5.6br(26), 4.6br(63)
o-tolyl	7.5m(53.2), 6.9m, 6.7m 2.54s(6.4)	4.58s	5.7m(c), 5.5m(c), 4.5m(64), 4.2m(60)

a) At room temperature. Chemical shifts are referred to internal TMS. Numbers in parentheses indicate J(Pt-H) in Hz. b) J(H-H)=7.6 Hz. c) Accurate values were not estimated due to extensive overlapping of the signals.

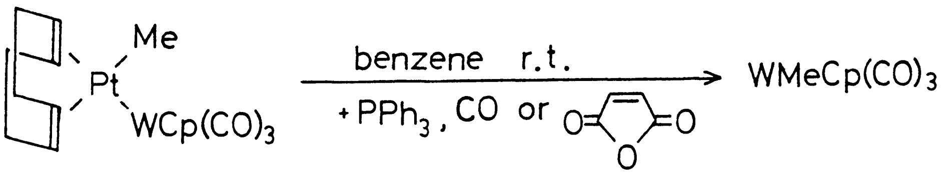
of the reaction, methyliodo(1,5-cyclooctadiene)platinum(II) as a reaction intermediate was detected in the ^{1}H NMR spectrum.

Thermolysis of **1** in C$_6$D$_6$ at 70 °C slowly afforded tricarbonyl(cyclopentadienyl)methyltungsten(II) in good yield(73% / **1**). The platinum product is supposed to be PtL$_n$. The result indicates that the methyl group migrates from the platinum moiety to the tungsten moiety. In other words, a reductive elimination of the methyl and the tungsten groups took place on the platinum metal.



The process is surprising, since generally cis-dialkylplatinum(II) complexes never give reductive elimination products. Such an alkyl migration in the heterodinuclear complex has been invoked in the metathetical reactions of organogold(III) complexes with anionic transition metal carbonyls.$^{7)}$

The alkyl migration was extraordinarily accelerated, when coordinating ligands were added. When triphenylphosphine(2.4 mol/**1**) or carbon monoxide (1 atm) were added to benzene solutions of **1** at room temperature, tricarbonyl(cyclopentadienyl)methyltungten(II) were obtained instantaneously in yields of 58 and 75%, respectively. Addition of maleic anhydride (2.5 mol/**1**) also induced the reaction (100%/**1**) in a day at room temperature.



An associative mechanism involving a five coordinate platinum species may explain the reaction. The detail kinetic study is under investigation. Similar unusual accelerating effects on the reductive elimination from transition metal dialkyls are known in the case of diarylbis(triphenylphosphine)platinum(II)$^{8)}$ and arylmethyl(1,2-bis(dimethylphosphino)ethane)nickel(II)$^{9)}$ complexes, although they are very rare.

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5) Yields: **1**, 73%. **2**, 40%. **3**, 42%. **4**, 34%. Mp: **1**, 105 °C. **2**, 52 °C. **3**, 129 °C. **4**, 140-142 °C. Satisfactory analytical data were obtained for **1**-**4**. Very low molar electric conductivity of **1** in THF($\Lambda \approx 0.0$ S cm^2 mol^{-1}) indicates its non-ionic structure.

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