Notes

Unexpected Formation of the Unique Complex Salt $[WI(CO)_2(PH_2CH_2Fc)_4]I$ [Fc = $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)$]

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Summary: The reaction of $[WI_2(CO)_3(NCMe)_2]$ *with an excess of* $FcCH_2PH_2$ [Fc = $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)$] *in THF leads to formation of the seven-coordinate pentanuclear complex salt* $[WI(CO)_2(PH_2CH_2Fc)_4]I$ (**1**), *while other compounds of the type* $[MI(CO)_2L_4]I$ *(with M = Mo, W and L =* PH_2Fc, PH_2CH_2Fc) *could not be obtained. The observation of this exceptional behavior was supported by quantum chemical calculations. Compound* **1** *is stable in the solid state, while an equilibrium between* **1**, $[WI_2(CO)_2(PH_2CH_2Fc)_3]$, *and* $FcCH_2PH_2$ *is observed in solution. The structure of the cation* $[WI(CO)_2(PH_2CH_2Fc)_4]^+$ *is an almost ideal trapezoidal octahedron, with the two CO ligands sharing one octahedral position.*

Introduction

Seven-coordinate molybdenum(II) and tungsten(II) complexes have been extensively studied. The first neutral halocarbonyl complex of a group 5 metal with a group 15 donor ligand, $[MoI_2(CO)_3(diars)]$ [diars = $1,2\text{-}(AsMe_2)_2C_6H_4$], was reported in 1957 by Nigam and Nyholm,[1] while the first structurally characterized ionic complexes involve the anion $[MI_3(CO)_4]^-$ (M = Mo, W), which apparently often forms in the presence of sterically demanding Brønsted bases (e.g., PPh_3) via intermolecular ligand exchange from $[MI_2(CO)_3(NCMe)_2]$. This anion is an example of a very regular capped octahedron whose noncapping CO ligands are evenly shifted from their ideal octahedral positions by the capping carbonyl ligand, which itself lies on a local C_3 axis.[2,3] The description of the cationic complex $[WI(CO)_2(cis\text{-}dppen)_2]I$ (dppen = bis(diphenylphosphino)ethene) by Baker et al.,[4] whose molybdenum analogue apparently could not be synthesized, gave rise to our more thorough investigations on the differences in reactivity between these two transition metals.

Recently, we described the synthesis of $[WI_2(CO)_3(PH_2CH_2Fc)_2]$,[5] the first structurally characterized tungsten(II) complex of a primary phosphine, which was formed when $[WI_2(CO)_3(NCMe)_2]$ was treated with 2 equivalents of $FcCH_2PH_2$ in CH_2Cl_2 at room temperature. Unexpectedly, we found that by applying a coordinating solvent like THF instead of the noncoordinating CH_2Cl_2, it was possible to replace one CO ligand in $[MI_2(CO)_3L_2]$ (M = Mo, W; L = PH_2Fc, PH_2CH_2Fc) by a third ferrocenylphosphine ligand and that this was the main reaction product in the case of M = Mo even when CH_2Cl_2 was used as solvent.[6] From our experiments, we inferred that molybdenum(II) tends to form tris-phosphine-substituted seven-coordinate complexes more readily than tungsten(II). Using quantum chemical calculations we were able to substantiate our experimental results. We now report the formation of a cationic seven-coordinate tungsten(II) complex of a primary ferrocenylphosphine with an unexpectedly large number of four monodentate phosphine ligands in the first coordination sphere of the tungsten atom, while the formation of a complex salt of the type $[MI(CO)_2L_4]I$ could not be observed either when $FcPH_2$ was used as a ligand or when the central atom was molybdenum.

Results and Discussion

Complexes of the type $[MI_2(CO)_2L_3]$ (M = Mo, W; L = PH_2Fc, PH_2CH_2Fc) are usually prepared by adding 3 equivalents of the ferrocenylphosphine to a solution of $[MI_2(CO)_3(NCMe)_2]$ in a coordinating solvent like THF. In most cases the results are identical if excess ferrocenylphosphine is applied.[6] However, when an excess of $FcCH_2PH_2$ was employed in the attempted synthesis of $[WI_2(CO)_2(PH_2CH_2Fc)_3]$, formation of $[WI(CO)_2(PH_2CH_2Fc)_4]I$ (**1**) was observed (Scheme 1). A similar exchange process has been observed between $[MX_2L_2]$ (M = Pt, Pd; X = Cl, Br; L = primary phosphine containing phenyl, cyclohexyl, or 2-cyanoethyl groups) and L, giving the complex salt $[MXL_3]X$.[7]

In the solid state, the cation in **1** lies on a crystallographic mirror plane that contains the $W(CO)_2I$ group (Figure 1). The tungsten atom is coordinated by four phosphine ligands in the equatorial plane, one iodo ligand in the axial position, and two carbonyl groups sharing the axial octahedral position opposite the iodo ligand. This structural motif is called a square-faced capped trigonal prism (*TPRS*-7),[8] "trapezoidal octahedron", or

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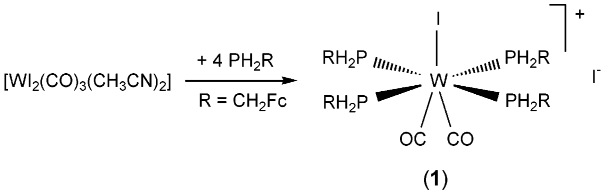
Scheme 1



(**1**)

Scheme 2

$$[WI(CO)_2(PH_2CH_2Fc)_4]I \rightleftharpoons [WI_2(CO)_2(PH_2CH_2Fc)_3] + PH_2CH_2Fc$$

"octahedral wedge". The unusual seven-coordinate octahedral wedge structure has rarely been observed in the literature and was mostly referred to only as a transition state.[9] Prerequisites for the formation of an ideal octahedral wedge are first four approximately equal donor ligands with a weak *trans* effect that are able to occupy the four equatorial positions, a single sterically demanding ligand to occupy one axial position, and two strongly *trans*-directing ligands to share the other axial position in such a way that no pentagonal plane is formed. The chelating bis-phosphine ligands in $[WI(CO)_2(\mathit{cis}\text{-dppen})_2]I$ exhibit similar P−W−P bond angles (P−W−P range from 71.99° to 76.26°)[4] to those observed in the cation of **1** (80.9°). It is noteworthy that only the cationic tungsten compound was obtained, while the molybdenum analogue apparently could not be synthesized.[4]

Compound **1** is stable in the solid state, while an equilibrium between **1**, $[WI_2(CO)_2(PH_2CH_2Fc)_3]$, and $FcCH_2PH_2$ is observed in solution (Scheme 2). Therefore, at room temperature solutions of **1** always show the resonances of the free ferrocenylmethylphosphine (−129.1 ppm) and the broad signals for $[WI_2(CO)_2(PH_2CH_2Fc)_3]$ (−55.2 ppm)[6] besides a signal for **1** at −54.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum. At lower temperatures, $[WI_2(CO)_2(PH_2CH_2Fc)_3]$ exhibits the known dynamic effects due to intramolecular ligand pseudorotation,[6] while no intramolecular ligand mobility is observed for **1** in the accessible temperature range. Attempts to prepare the corresponding complex salts of the type $[MI(CO)_2L_4]I$ were unsuccessful when either $FcPH_2$ was used as ligand or when the central atom was molybdenum. From simple mechanistic considerations the solitary formation of **1** could not be fully explained. While the different reactivity of the phosphine ligands $FcPH_2$ and $FcCH_2PH_2$ can be explained in terms of their steric demand (a larger Tolman cone angle[10] is expected for $FcPH_2$), the nonexistence of the molybdenum complex as opposed to the tungsten complex **1** is not easily explained.

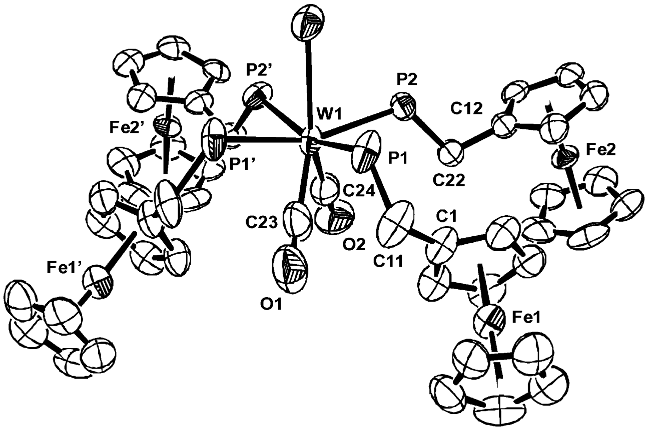


Figure 1. ORTEP view of the $[WI(CO)_2(PH_2CH_2Fc)_4]^+$ cation of **1**. All H atoms are omitted for clarity. Selected bond lengths (pm) and angles (deg): W(1)−I(1) 286.5(1), W(1)−P(1) 249.5(3), W(1)−P(2) 248.7(3), W(1)−C(23) 198(2), W(1)−C(24) 192(2), C(23)−O(1) 116(2), C(24)−O(2) 122(2), P(1)−W(1)−I(1) 80.14(8), P(2)−W(1)−I(1) 79.41(6), P(1)−W(1)−P(2) 80.9(1), P(1)−W(1)−P(1′) 95.1(1), P(1)−W(1)−P(2′) 159.5(1), P(2)−W(1)−P(1′) 159.5(1), P(2)−W(1)−P(2′) 95.8(1), C(23)−W(1)−I(1) 144.0(8), C(24)−W(1)−I(1) 146.8(5), C(23)−W(1)−P(1) 75.8(5), C(24)−W(1)−P(1) 120.1(3), C(23)−W(1)−P(2) 121.9(4), C(24)−W(1)−P(2) 78.5(3), C(23)−W(1)−C(24) 69.3(9).

We therefore evaluated energy profiles for the formation of the seven-coordinate model complexes $[MI(CO)_2(PH_3)_4]I$ (M = Mo, W) from $[MI_2(CO)_2(PH_3)_3]$ and PH_3 using state-of-the-art DFT calculations in which the rather large ferrocenyl-substituted phosphines were replaced by the model ligand PH_3 to gain insight into the reasons for the specific behavior of the compounds under study (for details of the calculations see the Supporting Information). Starting from $[MI_2(CO)_3(PH_3)_2]$ (M = Mo, W), the energy profiles for the substitution of a carbonyl ligand by a third phosphine were modeled. A dissociative reaction pathway, as proposed for the loss of the acetonitrile ligands in reactions between $[MI_2(CO)_3(NCMe)_2]$ and ligands with group 15 donors,[11] can be excluded, because activation energies of more than 100 kJ/mol are calculated. The substitution should proceed via an associative mechanism by a pseudorotation of the three CO groups followed by introduction of the third phosphine into an equatorial position and elimination of one CO from a capping position. Only for the molybdenum system is a low activation barrier obtained, which leads to a certain stabilization of the tris-phosphine-substituted product, in agreement with the experimental findings.[6]

Formation of the seven-coordinate complex salt **1** was modeled starting from $[MI_2(CO)_2(PH_3)_3]$ (M = Mo, W) and proceeding via eight-coordinate intermediates $[MI_2(CO)_2(PH_3)_4]$ (associative mechanism) or six-coordinate complex salts $[MI(CO)_2(PH_3)_3]^+$ (dissociative mechanism). Again, a dissociative mechanism can be excluded, because rather high activation energies are calculated. By combining the energy profiles of the associative mechanisms of the two reaction steps considered, it results that, for both molybdenum and tungsten, the seven-coordinate complex salt is destabilized in comparison to the starting model system $[MI_2(CO)_3(PH_3)_2]$. This is the case for the isolated systems corresponding to the gas phase as well as in solution. The latter was examined by applying a polarized continuum model. Consequently, the exceptional behavior resulting in formation of **1** should be a consequence of the peculiarities of the ferrocenyl-substituted phosphines (compared to PH_3) and/or specific interactions (packing effects) in the solid state.

Experimental Section

General Details. All reactions were carried out under nitrogen using standard Schlenk line techniques. Solvents were dried and distilled under an inert gas atmosphere prior to application. The primary ferrocenylphosphines PH_2Fc[12] and PH_2CH_2Fc[13] were prepared according to the literature procedures and purified by

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sublimation. The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W)[14] were recrystallized from CH_2Cl_2 prior to use.[6] NMR spectra were recorded in $CDCl_3$ at 25 °C (if not stated otherwise) using an Avance DRX 400 spectrometer (Bruker). NMR tubes were filled under nitrogen and sealed under vacuum. ^1H NMR (400 MHz) spectra were calibrated against TMS, using $CDCl_3$ as an internal standard. ^{31}P NMR (161.7 MHz) spectra were calibrated against 85% H_3PO_4 as an external standard. The IR spectra (4000−400 cm^{-1}) of the solid complex in KBr disks were recorded on a Perkin-Elmer Spectrum 2000 FTIR spectrometer. Elemental analysis was performed on a VARIO EL (Heraeus) with handling of the samples in air. The melting point was determined in a sealed capillary under nitrogen and is uncorrected.

$[WI(CO)_2(PH_2CH_2Fc)_4]I$ (1). $[WI_2(CO)_3(NCMe)_2]$ (0.36 g, 0.60 mmol) and $FcCH_2PH_2$ (0.60 g, 2.58 mmol) were dissolved in THF (20 mL) and stirred for 24 h. The solution was filtered over degassed Celite and dried in vacuo. The crude product was washed twice with *n*-pentane (20 mL). The residue was redissolved in CH_2Cl_2 and precipitated with *n*-pentane. After sedimentation the solvent was removed with a pipette, and the residue was dried in vacuo for 1 h. The remaining orange powder was dissolved in CH_2Cl_2 (20 mL). After 2 days at −30 °C orange crystals suitable for X-ray crystal structure analysis were obtained. Yield: 0.96 g (89%) of **1**$\cdot 4.5CH_2Cl_2$. Mp: 82−84 °C (dec). Anal. Found: C, 33.80; H, 3.56, O, 1.81 (Calcd C, 33.62; H, 3.41; O, 1.77). ^1H NMR (**1** recrystallized from THF): 1.85 and 3.75 ppm (each m, 3 H each, THF), 2.62 ppm (br, 2 H, CH_2 in free $FcCH_2PH_2$), 3.17 ppm (br, 6 H, CH_2), 4.07, 4.13, and 4.17 ppm (br, 36 H, η^5-C_5H_5 and η^5-C_5H_4), 5.45 ppm (br d, $^1J_{P-H}$ = 368 Hz, 6 H, PH_2), PH_2 in free $FcCH_2PH_2$ not visible. ^{31}P NMR: −54.6 ppm (t, $^1J_{P-H}$ = 160 Hz), −55.2 ppm (br, $[WI_2(CO)_2(PH_2CH_2Fc)_3]$), −129.1 ppm (br, $FcCH_2PH_2$). IR (cm^{-1}): 3089 m, 2963 m, 2330 m, 1952 s, 1889 s, 1633 m, 1462 w, 1408 m, 1262 w, 1238 w, 1204 w, 1104 s, 1038 m, 1023 m, 1000 m, 969 w, 922 m, 872 m, 819 m, 730 w, 592 w, 545 w, 481 m, 424 w.

Density Functional Theory (DFT) Calculations. DFT calculations with the widely used B3LYP functionals[15−17] were performed using the Gaussian03 program package.[18] For the metal atoms and for iodine, relativistic effective core potentials replacing the 10 and 50 inner core electrons, respectively, and the corresponding valence basis sets were used.[19] The standard 6-31g(d) basis set was applied for the other atoms.[20] The stationary points resulting from the optimizations were characterized by frequency analysis. The influence of a solvent (tetrahydrofuran) was considered with a polarized continuum model.[21]

Table 1. Crystal Data and Intensity Collection and Refinement Details for $[WI(CO)_2(PH_2CH_2Fc)_4]I$ (1)

lattice	orthorhombic	*Z*	8
formula	$C_{46}H_{52}Fe_4I_2O_2P_4W\cdot 4.5CH_2Cl_2$	temp, K	208(2)
fw	1803.97	ρ(calcd), g cm^{-3}	1.825
space group	*Ibam*	μ(Mo Kα), mm^{-1}	4.047
a, Å	16.799(2)	θ_{max}, deg	26.37
b, Å	25.767(4)	no. of data	41 733
c, Å	30.342(3)	no. of params	359
V, Å^3	13 134(3)	R1 [$I < 2\sigma(I)$]	0.0613
wR2 [$I < 2\sigma(I)$]	0.1551	R1 (all data)	0.1093
wR2 (all data)	0.1826	GOF	1.076

X-ray Analysis. The data were collected on a Siemens CCD diffractometer (SMART) using Mo Kα radiation (λ = 71.073 pm) and ω-scan rotation. Data reduction was performed with SAINT including the program SADABS for empirical absorption correction. Details are given in Table 1. The structure was solved by heavy-atom methods, and the refinement of all non-hydrogen atoms was performed with SHELX97. H atoms were calculated on idealized positions. Structure figures were generated with ORTEP.[22] CCDC 637643 (**1**) contains the supplementary crystallographic data for this paper. The 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).

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Supporting Information Available: VT ^{31}P NMR spectra of **1**; attempts to prepare the corresponding compounds $[MoI(CO)_2(PH_2CH_2Fc)_4]I$, $[MoI(CO)_2(PH_2Fc)_4]I$, and $[WI(CO)_2(PH_2Fc)_4]I$; details of the DFT calculations including energy profiles for the different mechanisms. This material is available free of charge via the Internet at http://pubs.acs.org.

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