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TRANSITION METAL σ-2-OXOALKYL COMPLEXES

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Summary

Preparations of tricarbonyl(h^1-2-oxopropyl)-molybdenum and -tungsten compounds and tricarbonyl(h^1-2-oxoethyl)molybdenum are described. Preparations of acetylacetonato bis(h^2-trimethylsiloxyethylene)rhodium and 1,3-dichloro-μ-dichloro-2,4-bis(h^2-trimethylsiloxyethylene)dipalladium are described with attempts at hydrolytic cleavage.

Introduction

In connection with our studies of the interconversion of h^1-2-oxoalkyl- and h^2-hydroxyalkenyl-metal complexes via $\sigma \to \pi$ rearrangement, we have prepared new h^1-2-oxoalkyl derivatives of molybdenum and tungsten directly and have under taken the preparation of analogous compounds of palladium and rhodium indirectly via both $\pi \to \sigma$ rearrangement and ligand exchange processes. While the indirect synthetic routes were not successful, several interesting new h^2-alkenyl derivatives of palladium and rhodium were prepared and two new reactions of chloro(acetylacetonato)(h^2-hydroxyethylene)platinum (XI) were observed.

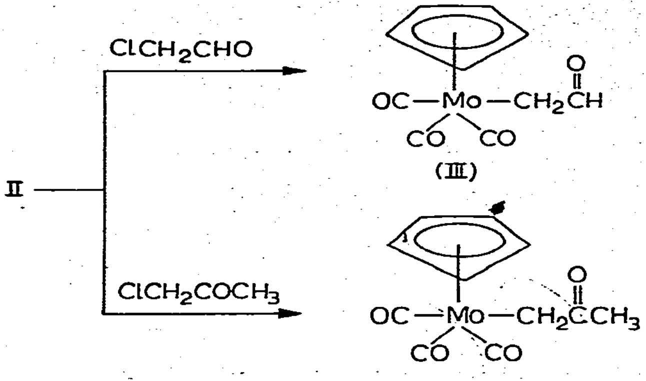
Results and discussion

Direct preparation of h^1-2-oxoalkyl-molybdenum and -tungsten complexes

The molybdenum derivatives were prepared by the method reported by Ariyaratne and Green for dicarbonyl(h^5-cyclopentadienyl)(h^1-2-oxoethyl)iron [1] in which the tricarbonyl(h^5-cyclopentadienyl)molybdenum dimer (I) in tetrahydrofuran was reductively cleaved over sodium amalgam to produce the sodium salt of tricarbonyl(h^5-cyclopentadienyl)molybdenum (II), which was treated with either chloroacetaldehyde or chloroacetone to produce the h^1-2-oxoethyl (III) and h^1-2-oxopropyl (IV) compounds, respectively.

The tungsten derivative, tricarbonyl(h^5-cyclopentadienyl)(h^1-2-oxopropyl)-tungsten (VII) was also prepared via the sodium salt (VI). Treatment of tungsten

$$\underset{(I)}{[C_5H_5Mo(CO)_3]_2} \xrightarrow[Na/Hg]{THF} \underset{(II)}{[C_5H_5Mo(CO)_3]Na}$$



(III)

(IV)

hexacarbonyl (V) with sodium cyclopentadienide in tetrahydrofuran produced the salt VI which was in turn treated with chloroacetone, yielding (VII).

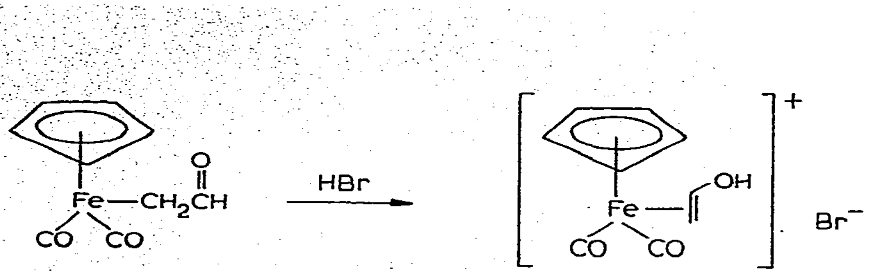
$$\underset{(V)}{W(CO)_6} + C_5H_5Na \xrightarrow{THF} \underset{(VI)}{C_5H_5W(CO)_3Na}$$

(VII)

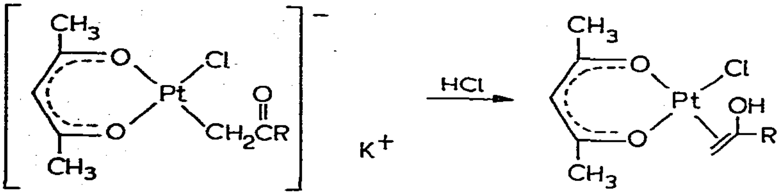
Since the h^1-2-oxoethyliron analog (VIII) [1] and the platinum complexes (X) and (XII) [2] have been reported to undergo protonation, producing the π-vinyl alcohol complexes (IX), (XI) and (XIII), respectively, attempts were made to protonate the h^1-2-oxopropyl complexes of molybdenum (IV) and tungsten (VII). These attempts were unsuccessful, since apparently any mineral acid strong enough to protonate these weakly basic compounds were also strong enough to decompose them.

Attempted indirect preparation of h^1-2-oxoalkyl-palladium, -rhodium and -platinum complexes via the vinyl ether compound

The method for preparing (h^2-hydroxyethylene)metal complexes which has been most widely utilized thus far has involved the synthesis and subsequent hydrolysis of a (h^2-trimethylsiloxyethylene) intermediate. Wakatsuki, Nozakura, and Murahasi [3] reported the preparation of 1,3-bis(h^2-hydroxyethylene)-2,4-



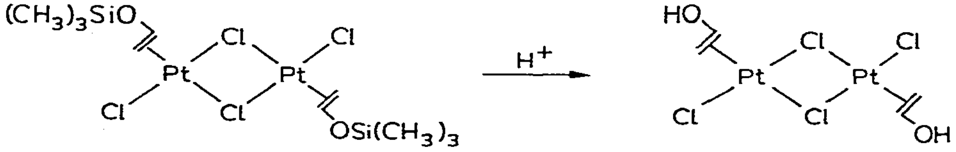
(VIII) (IX)



(X) R = H
(XII) R = CH_3

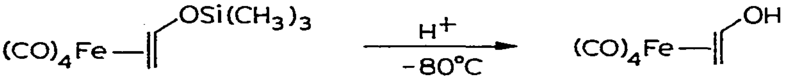
(XI) R = H
(XIII) R = CH_3

dichloro-μ-dichlorodiplatinum (XV) via the trimethylsiloxyethylene complex (XIV).



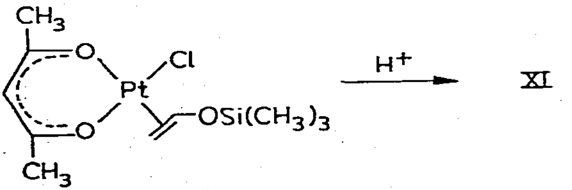
(XIV) (XV)

Thyret [4] reported a similar synthesis of tetracarbonyl(h^2-hydroxyethylene)-iron (XVII) at low temperature via hydrolysis of the trimethylsiloxyethene complex (XVI).



(XVI) (XVII)

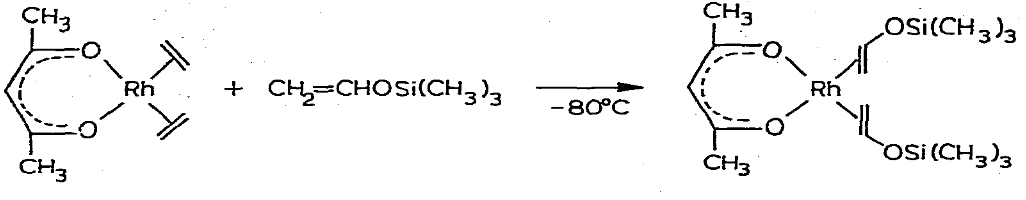
The first reported preparation by Tsutsui, Ori and Francis of chloro(acetylacetonato)(h^2-hydroxyethylene)platinum (XI) also employed a trimethylsiloxyethylene intermediate (XVIII) [2].



(XVIII)

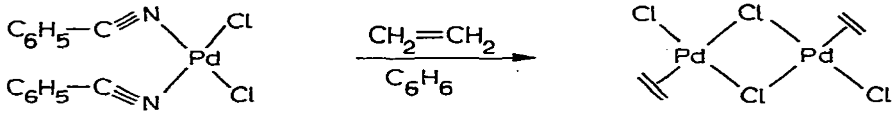
With the above syntheses in mind together with the fact that in polar solvents the h^1-2-oxoethyl- and h^2-hydroxyethylene-platinum compounds (X and XI) exist in equilibrium and can be interconverted by changing the pH of the medium [2], the preparation of h^2-trimethylsiloxyethylene ether complexes of palladium and rhodium was undertaken with the intention of preparing the corresponding h^2-hydroxyethylene complexes by hydrolysis, and then converting these to h^1-2-oxoethyl compounds in dilute alkali.

Treatment of (acetylacetonato)bis(h^2-ethylene)rhodium (XIX) [5] with trimethylsiloxyethylene at low temperature, produced (acetylacetonato)bis(h^2-trimethylsiloxyethylene)rhodium (XX) in good yield.

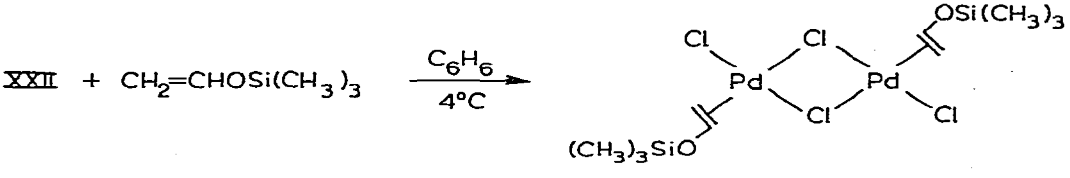


(XIX) (XX)

Dibenzonitrilepalladium dichloride (XXI) was converted to 1,3-dichloro-μ-dichloro-2,4-di-h^2-ethylenedipalladium (XXII) by treatment with ethylene gas in benzene solution and the ethylene complex was converted to 1,3-dichloro-μ-dichloro-2,4-bis(h^2-trimethylsiloxyethylene)dipalladium (XXIII) on treatment with trimethylsiloxyethylene in cold benzene.



(XXI) (XXII)



(XXIII)

Attempts to hydrolyze the vinyl ether compounds were unsuccessful, leading to complete decomposition.

Experimental section

All manipulations were carried out under dry argon. All solvents were distilled from appropriate drying agents, degassed and stored under argon. Unless otherwise specified column chromatography was carried out under argon using Fisher alumina adjusted to Brockman Activity II (3% water). Where melting points are not given, the compound was observed to decompose above room temperature. IR spectra were obtained using Perkin—Elmer 237 and Beckman IR-8 spectrometers. NMR spectra were recorded using Perkin—Elmer EM 360 and Varian T-60 spectrometers. Elemental analyses were done by Schwartzkopf Microanalytical Laboratories, Woodside, New York and Galbraith Laboratories, Knoxville, Tennessee.

Preparation of tricarbonyl(h^5-cyclopentadienyl)(h^1-2-oxoethyl)molybdenum (III)

A solution of 1.00 g (2.04 mmol) of tricarbonyl(h^5-cyclopentadienyl)molybdenum dimer in 30 ml of tetrahydrofuran was reductively cleaved over an excess of 2% sodium amalgam. After the excess amalgam had been drawn off, the reaction mixture was cooled to —80°C and a solution of 1 ml of chloroacetaldehyde in 10 ml of ether was added. The solution was allowed to warm to room temperature and stirred for three hours, after which the solvent was removed in vacuo and the residue extracted with ether. The ether solution was chromatographed on an alumina column. Elution with ether produced a yellow forerun followed by a second yellow band which produced a brown yellow solid tricarbonyl(h^5-cyclopentadienyl)(h^1-2-oxoethyl)molybdenum, 837 mg, m.p. 175°C, dec. (71.2%). Found: C, 41.68; H, 2.88; Mo, 33.06. $C_{10}H_8MoO_4$ calcd.: C, 41.66; H, 2.78; Mo, 33.33%. IR (neat) ν (cm^{-1}): 2020, 1945, 1900 (m-CO); 1648 (C—CH=O), 830 (C_5H_5); NMR (CS_2) τ (ppm) 8.20 (d, 2, CH_2), 4.80 (s, 5, C_5H_5), 0.65 (t, 1, CH=O).

Preparation of tricarbonyl(h^5-cyclopentadienyl)(h^1-2-oxopropyl)molybdenum(IV)

A solution of 1.00 g (2.04 mmol) of tricarbonyl(h^5-cyclopentadienyl)molybdenum dimer in 30 ml of tetrahydrofuran was reduced over excess 2% sodium amalgam and treated with 1.0 ml of chloroacetone (added drop by drop) at —40°C as described previously. After three hours at room temperature, the solvent was removed and the residue taken up in ether and chromatographed on an activity III alumina column. Elution with ether/petroleum ether (2 : 1) produced a brown forerun followed by a pale-yellow band. Evaporation of the yellow band to dryness yielded 831 mg of the waxy brown tricarbonyl(h^5-cyclopentadienyl)(h^1-2-oxopropyl)molybdenum (67.5%). Found: C, 43.91; H, 3.40; Mo, 30.99. $C_{11}H_{10}MoO_4$ calcd.: C, 43.72; H, 3.31; Mo, 31.77%. IR (neat) ν (cm^{-1}) 2000 (Mo—CO), 1650 (C=O); NMR (CS_2) τ (ppm) 9.30 (5, 2, CH_2), 8.00 (s, 3, CH_3), 4.64 (s, 5, C_5H_5).

Preparation of tricarbonyl(h^5-cyclopentadienyl)(h^1-2-oxopropyl)tungsten (VII)

A solution of 10.0 g (28.4 mmol) of tungsten hexacarbonyl in 30 ml of tetrahydrofuran was mixed with 24 ml of a 2.6 *M* solution of sodium cyclopentadienide in tetrahydrofuran (62.4 mmol) and refluxed for 24 hours. Evaporation of the solvent in vacuo yielded 6.50 g (18.3 mmol) of bright yellow solid sodium tricarbonyl(h^5-cyclopentadienyl)tungsten. A solution of 4.20 g (11.8 mmol) of sodium tricarbonyl(h^5-cyclopentadienyl)tungsten in 40 ml of tetrahydrofuran was cooled to —80°C, a 2.00 ml portion of chloroacetone was added, and the solution stirred at room temperature for two hours. The solvent was removed in vacuo and the residue extracted with ether. The ether solution was chromatographed on an activity III alumina column. Elution with ether produced a yellow band and removal of the solvent from this band produced 2.81 g (7.21 mmol) of red-yellow waxy solid tricarbonyl(h^5-cyclopentadienyl)(h^1-2-

oxopropyl)tungsten (61.1%). Found: C, 34.28; H, 2.15; W, 42.52 $C_{11}H_{10}O_4W$ calcd.: C, 33.85; H, 2.56; W, 43.58%. IR (neat) ν (cm^{-1}), 2025, 1925 (W—CO), 1700 (C=O); NMR ($CDCl_3$) τ (ppm) 7.90 (s, 3, CH_3), 7.70 (s, 2, CH_2), 4.50 (s, 5, C_5H_5).

Attempted protonation of tricarbonyl(h^5-cyclopentadienyl)(h^1-2-oxopropyl)molybdenum (III)

Treatment of this compound with hexafluorophosphoric acid in ether and dilute hydrogen chloride gas in petroleum ether resulted in decomposition and no reaction respectively.

Attempted protonation of tricarbonyl(h^5-cyclopentadienyl)(h^1-2-oxopropyl)tungsten (VII)

Treatment of this compound with dilute anhydrous hydrogen chloride gas dissolved in petroleum ether resulted in complete decomposition.

Preparation of (acetylacetonato)bis(h^2-trimethylsiloxyethylene)rhodium (XX)

A 0.203 g (0.867 mmol) portion of (acetylacetonato)di-h^2-ethylenerhodium [5] was combined with 0.250 ml of trimethylsiloxyethylene at −80°C and stirred for three hours at room temperature. The solution was centrifuged and the clear solution was allowed to stand at 0°C. After twelve hours, a yellow precipitate was collected and recrystallized from hexane, yielding 233 mg (0.538 mmol) (62%) of (acetylacetonato)bis(h^2-trimethylsiloxyethylene)rhodium, m.p. 79.5—80.5°C. Found: C, 41.57; H, 7.41; Rh, 23.34. $C_{15}H_{31}O_4RhSi_2$ calcd.: C, 41.47; H, 7.19; Rh, 23.68%. IR(KBr) ν (cm^{-1}): 1570, 1520 (C—O···Rh···O—C), 1490, 1380, 1250, 1260, 1152 (Si—O) 995, 981 (Si—O); NMR (benzene-d_6) τ (ppm) 9.70 (s, 18, $Si(CH_3)_3$), 8.20 (s, 6, $O{=}CH_3$), 7.05 (m, 4, $CH_2{=}$), 4.88 (s, 1, $O{=}CCHC{=}O$), 3.68 (m, 2, $=CHOSi$).

Preparation of 1,3-dichloro-μ-dichloro-2,4-bis(h^2-trimethylsiloxyethylene)dipalladium (XXIII)

Dry ethylene gas was bubbled through a solution of 535 mg (1.40 mmol) of dibenzonitrile palladium dichloride [6] in 10 ml of dry benzene and yellow crystals formed. A total of 160 mg (0.389 mmol), 55.7% yield) of 1,3-dichloro-μ-dichloro-2,4-di-h^2-ethylenedipalladium was collected and dried briefly under vacuum (the complex looses ethylene easily). The diethylenedipalladium complex was then treated with a solution of 0.40 ml of trimethylsiloxyethylene in 3.0 ml of dry benzene at 4°C. After effervescence had ceased, the reaction mixture was triturated with dry hexane and centrifuged. The yellow-brown precipitate was separated from the decantate and dried under vacuum. A total of 102.8 mg (0.350 mmol) of 1,3-dichloro-μ-dichloro-2,4-bis(h^2-trimethylsiloxyethylene)dipalladium, or 90% yield based on the ethylene complex, was obtained (reprecipitated from benzene—hexane). Found: C, 20.57; H, 4.14. $C_{10}H_{24}Cl_4O_2Pd_2Si_2$ calcd.: C, 20.40; H, 4.12%. IR (nujol) ν (cm^{-1}): 1500 (C=C), 1050 (C—O); NMR (benzene-d_6) τ (ppm) 9.74 (s, 3, $Si{-}CH_3$), 6.07 (t, 2 $=C{<}^{H}_{H}$), 2.28 (m, 1, $\equiv SiOCH{=}$), *J*(*trans*-$CH_2{=}CHO$) 11.6 Hz, *J*(*cis*) 3.8 Hz.

Attempted hydrolysis of (acetylacetonato)bis(h^2-trimethylsiloxyethylene)-rhodium

This compound did not react with moist argon, moist ether, or moist benzene and only decomposition was observed upon treatment with trifluoroacetic acid in ether and dilute hydrochloric acid in tetrahydrofuran.

Attempted hydrolysis of tetrachloro-bis(h^2-trimethylsiloxyethylene)dipalladium

This compound decomposed on treatment with moist argon, moist ether trifluoroacetic acid in ether, moist benzene and dilute hydrochloric acid in tetrahydrofuran, producing only black, metallic residue.

Acknowledgment

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