

Transition Metal Methylene Complexes, XXVII¹⁾**Synthesis of the First Heavy-Metal Substituted μ -Methylene Complex**

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Übergangsmetall-Methylen-Komplexe, XXVII¹⁾**Synthese des ersten schwermetallsubstituierten μ -Methylen-Komplexes**

Die Umsetzung des cycloadditionsaktiven zweikernigen Carbonylrhodium-Komplexes **1** mit dem Diazoquecksilber-Substrat **2** ergibt unter rascher N_2 -Eliminierung (THF, $-70^\circ C$) die in Substanz isolierbare Verbindung **3** als erstes Beispiel schwermetallsubstituierter μ -Methylen-Komplexe.

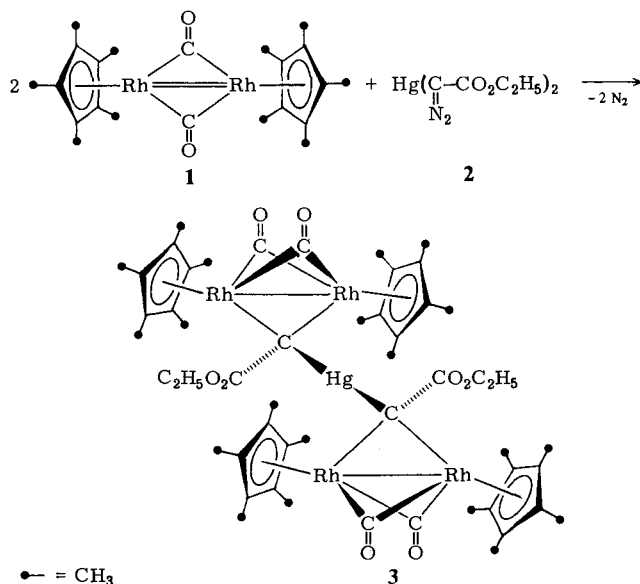
The reaction of diazoalkanes with unsaturated transition metal complexes is one of the most general synthetic methods available for the preparation of dimetallacyclopropane-type μ -methylene complexes²⁾. The best metal substrates for these reactions very likely are complexes having metal-metal multiple bonds, which can add to the alkylidene fragment with only minimal changes in coordination geometry and without expulsion of a ligand. We have now succeeded in employing this method in the synthesis of the first heavy-metal substituted μ -methylene compound, $[\mu_3-C-(CO_2C_2H_5)\{\eta^5-C_5Me_5\}Rh(\mu-CO)]_2Hg$ (**3**). This easily accessible complex now represents a promising starting point for methylene bridge homologation using electrophilic reagents, chemistry that has been established for *Buchner's* old diazo precursor $Hg[C(=N_2)CO_2C_2H_5]_2$ (**2**)³⁾ by the *Schöllkopf* group^{4,5)}.

Bis[diazo(ethoxycarbonyl)methyl]mercury (**2**) reacts with the dinuclear carbonylrhodium complex **1** even at $-70^\circ C$ in tetrahydrofuran to give the diamagnetic, neutral compound **3** in nearly quantitative yield. Chromatography on Florisil with subsequent crystallization allows to isolate analytically pure **3** as a purple solid. Although crystalline samples may be handled briefly in air without noticeable decomposition (IR, **3** is very air-sensitive in solution (hydrocarbons, diethyl ether, tetrahydrofuran, aromatic solvents); rapid decomposition occurs, even in the absence of oxygen, in halogenated solvents such as chloroform.

The novel μ -mercuriomethylene complex was characterized by elemental analysis, IR and ¹H NMR spectroscopy. The infrared absorptions at 1820 and 1765 cm^{-1} (KBr) are typical of metal-to-metal carbonyl bridges and very much resemble those of the structurally well established compounds of type $(\mu-CRR')\{\eta^5-C_5Me_5\}Rh(\mu-CO)_2$ (e. g., $CRR' =$ tetrabromocyclopentadienylidene^{1,2a,6)}); in addition, the ester function gives rise to a characteristic absorption at 1695 cm^{-1} (KBr)⁷⁾. The ¹H NMR spectra are in accord with the crowded structure as indicated in formula **3** (two sets of equivalent C_5Me_5 protons). Confirmation of the molecular weight of **3** proved

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impossible by mass spectrometry, neither by ion impact nor by field desorption methods, yielding instead the known derivative $[\mu\text{-CH}(\text{CO}_2\text{C}_2\text{H}_5)][(\eta^5\text{-C}_5\text{Me}_3)\text{Rh}(\text{CO})_2]^{1,2\text{a},6)}$ as a result of decomposition under the conditions required for these measurements. However, a proper molecular weight determination was obtained by osmometry under scrupulously air-free conditions.



The reaction leading to **3** demonstrates that heavy-metal substituted μ -methylene complexes (a) can be prepared by the same method as the conventional members of this series^{2a,b,6,8)} and, (b) display reasonable thermal stability facilitating investigation of their chemistry. Only mercury-free μ -methylidyne complexes have so far been accessible from α -mercuriodiazoalkanes⁹⁾.

Experimental Part

All manipulations were conducted with careful exclusion of oxygen and water using standard Schlenk techniques. All solvents were thoroughly dried by refluxing over Na/K alloy or phosphorus pentoxide, resp., and were stored under nitrogen. — IR: Beckman Infrared Grating Spectrophotometer 4240. — ¹H NMR: Bruker WH-90. — **1** was prepared as described in the literature^{1,6)} from $[\eta^5\text{-C}_5(\text{CH}_3)_3]\text{Rh}(\text{CO})_2$; the α -mercuriodiazoalkane **2** was obtained through H/Hg replacement from ethyl diazoacetate using red mercury oxide^{3,5)}. Elemental analyses were carried out in the Mikroanalytische Laboratorien, vorm. A. Bernhardt, D-5270 Gummersbach/Elbach 1.

Mercurybis[μ_3 -(ethoxycarbonylmethylidyne)-bis(μ -carbonyl)-(η^5 -pentamethylcyclopentadienyl)-rhodium(Rh-Rh)] (**3**): A solution of **2** (193 mg, 0.45 mmol) in 5 ml of tetrahydrofuran was added to a magnetically stirred suspension of **1** (483 mg, 0.91 mmol) in 20 ml of the same solvent cooled to -70°C . Immediate N_2 evolution with concomitant color change from blue to rust-red was observed. The solution was allowed to warm up to room temperature over ca. 60 min; the solvent was then removed in vacuo. The resulting deep purple residue was subjected to column chromatography on Florisil (Merck, 100–200 mesh ASTM; column dimensions 30×1.5 cm; watercooled jacket, ca. 15°C) eluting first with toluene traces of unreacted **2**, then with THF/toluene (1:1) compound **3** as a purple band. Some decomposed products remain at the origin.

Removal of the solvent in vacuo yielded 621 mg (95%) of **3** as a purple solid. Subsequent crystallization from a minimum amount of diethyl ether (-78°C) gave dark purple lustrous crystals consisting of multiple planes. M. p. 145°C (dec., sealed tube). — IR: (THF) 1820 m, 1785 w (sh), 1770 s, 1700 cm^{-1} m; (KBr) 1820 m, 1765 s-vs, 1695 cm^{-1} m. — ^1H NMR ($[\text{D}_6]$ benzene, int. TMS, 25°C): CH_3 , ester $\delta = 1.18$ [t, 3H; $^3J_{\text{H,H}} = 7.0$ Hz], CH_3 , C_5Me_5 1.25 and 1.82 ("s", equal intensity, total int. 30H), CH_2 , ester 4.17 [q, 2H; broadened signal]. — Conductivity: $\Lambda = 6 \text{ cm}^2 \cdot \text{mol}^{-1} \cdot \Omega^{-1}$ (non-electrolyte; benzene, $c = 10^{-3} \text{ mol/l}$, $T = 15.1^{\circ}\text{C}$).

$\text{C}_{52}\text{H}_{70}\text{HgO}_8\text{Rh}_4$ (1435.3) Calc. C 43.51 H 4.92 Hg 13.97 N 0.00 Rh 28.68
 Found C 43.41 H 4.89 Hg 13.77 N <0.2 Rh 28.72
 Mol. weight 1400 ± 50 (osmometrically in benzene)

Immediate crystallization of the crude product (see above) without chromatography gives slightly impure samples that decompose in the range $135 \dots 140^{\circ}\text{C}$ although IR spectra are practically identical with those obtained from chromatographed samples. Nitrogen and mercury analyses show that the composition of **3** does not change during chromatography on florisil (N, 0%; Hg, 13.65%); moreover, the initial product has the same structure (IR) as the chromatographed product.

- 1) This work was gratefully supported by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, *Degussa Hanau*, *Chemische Werke Marl Hüls*, and the *Alexander von Humboldt-Stiftung*. — For Communication XXVI, see: W. A. Herrmann, J. Plank, Ch. Bauer, M. L. Ziegler, E. Guggolz, and R. Alt, *Z. Anorg. Allg. Chem.*, in press.
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