In the experiments performed in the present paper, the possibility that the rapid activation of molecular hydrogen occurs via the small quantity of **6** in the system (which is in equilibrium with **1**) can be discounted. It is known[19] that **6** reacts with hydrogen in the absence of dissolved carbon monoxide; however, the rate per mole of complex under otherwise identical conditions is more than 1 order of magnitude slower. Further, it has been shown that, in the presence of carbon monoxide, **6** transforms to **1** before H_2 activation in the system occurs.[12,19]

A truly elegant, but technically difficult experiment, for the reaction of hydrogen in the **6**, **1**, and **7** system remains to be performed, e.g., the determination of the apparent activation energy E_{app} for the activation of molecular hydrogen in the presence of **7**. Given a sufficiently high partial pressure of carbon monoxide (i.e., $P_{CO} \geq 20$ MPa) and a low enough reaction temperature (i.e., $T \leq 258$ K), nearly quantitative conversion of **1** to **7** (>97%) will occur. Reaction of hydrogen under these conditions could be anticipated to give a measured apparent activation energy E_{app} equal to approximately 50 kJ/mol, that is, the enthalpy of reaction for the formation of **1** from **7** (24 kJ/mol) plus the actual activation energy E_a for hydrogen dissociation on **1**.

Acknowledgment. This work was supported by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forchung. The starting material $Co_2Rh_2(CO)_{12}$ used in this study was synthesized by Dr. I. T. Horváth. Discussions with Professors L. Venanzi and G. Consiglio are greatly appreciated.

Registry No. $CoRh(CO)_7$, 78714-10-0; H_2, 1333-74-0; CO, 630-08-0.

Conversion of Metallacyclic Zirconoxycarbene Complexes Yielding Conventional Fischer-Type Carbene Complexes or Metal-Free Organic Products

Gerhard Erker* and Friedrich Sosna

Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, FRG

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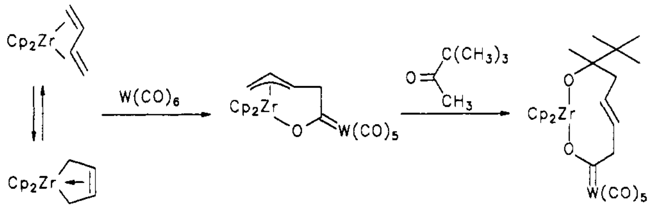
Reaction of (butadiene)zirconocene with hexacarbonyltungsten yields the metallacyclic (π-allyl)zirconoxycarbene complex $Cp_2\overline{ZrOC[{=}W(CO)_5]C}{}_4H_6$ (**2**). Subsequent coupling with pinacolone gives the nine-membered metallacycle *trans*-$Cp_2\overline{ZrOC[{=}W(CO)_5]CH_2CH{=}CHCH_2CMe(CMe_3)O}$ (**3**). Both compounds **2** and **3** show a very low Fischer carbene complex reactivity. Hydrolytic removal of the zirconocene moiety transforms the rather unreactive zirconoxycarbene complexes into conventional heteroatom-stabilized transition-metal carbene complexes. Thus, treatment of **3** with water in tetrahydrofuran generates a hydroxycarbene tungsten complex in situ, which is efficiently trapped by added excess diazomethane to yield the enol ether $H_2C{=}C(OCH_3)CH_2CH{=}CHCH_2CMe(CMe_3)OH$ as the major reaction product. Similarly, controlled hydrolysis of **3** in the presence of pyridine *N*-oxide gives $HOOCCH_2CH{=}CHCH_2CMe(CMe_3)OH$. The reaction of **3** with tetra-*n*-butylammonium fluoride trihydrate in tetrahydrofuran cleaves the metallacycle to give a zirconium-free acylmetallate anion (Bu_4N^+ counterion) which is readily O-alkylated by using Meerwein's reagent to produce $H_5C_2OC[{=}W(CO)_5]CH_2CH{=}CHCH_2CMe(CMe_3)OH$ (**11**, ca. 70% overall yield). Similarly, the zirconoxycarbene complex **2** yields $H_5C_2OC[{=}W(CO)_5]CH_2CH{=}CHCH_3$ upon treatment with $Bu_4NF(H_2O)_3$ followed by alkylation with $(H_5C_2)_3OBF_4$.

Introduction

Many metal carbonyl complexes can readily be converted to heteroatom-stabilized carbene complexes by reacting them with a variety of (olefin)group 4 metallocene type reagents.[1] This essentially nonnucleophilic alternative to the conventional Fischer synthesis[2] often gives high yields of the corresponding metallacyclic titano-, hafnio-, or zirconoxycarbene complexes. The reaction of the (*s-cis/s-trans*-η^4-butadiene)zirconocene system with hexacarbonyltungsten is a typical example, cleanly giving the carbene complex **2**[3] (Scheme I). Subsequent addition of an organic carbonyl compound (here pinacolone) to the (π-allyl)zirconocene unit selectively converts **2** to the nine-membered metallacyclic zirconoxycarbene complex

Scheme I



1 2 3

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[1] (a) Erker, G. Carbene Complex Synthesis with Group 4 Metallocene Reagents. In de Meijere, A., Tom Dieck, H., Eds. *Organometallics in Organic Synthesis*; Springer Verlag: Berlin, 1988. (b) Erker, G. *Angew. Chem.* **1989**, *101*, 411; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397.

[2] Fischer, E. O.; Maasböl, A. *Angew. Chem.* **1964**, *76*, 645; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

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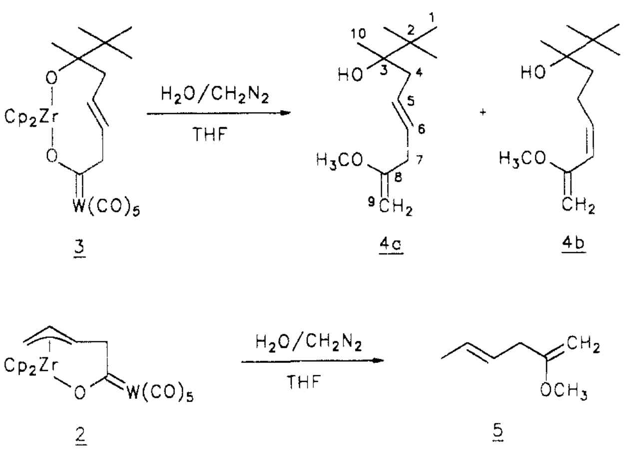
Scheme II



3 (only one diastereomer with (2R^*)(4,5,6-pS^*) relative configuration found).[4]

The zirconoxycarbene complexes **2** and **3** have a much reduced carbene complex reactivity as compared to normal O-alkylated Fischer-type carbene complexes. For example, **3** does not appear to react with amines, enol ethers, simple alkenes or alkynes, or even diazomethane up to its decomposition temperature (ca. 80 °C). Only strongly basic reagents such as butyllithium or $Ph_3P{=}CH_2$ react with **3** even at low temperature, cleaning resulting in α-deprotonation.[5]

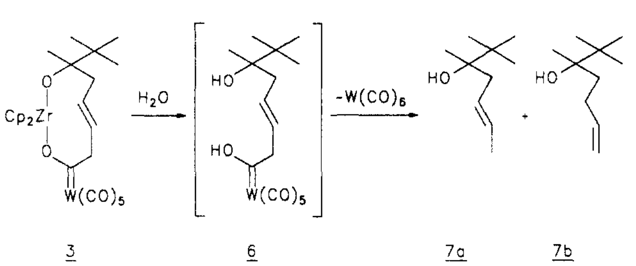
The low electrophilic reactivity of the metal carbene moiety in complexes **2** and **3** underlines the pronounced metal acyl type character of the zirconoxycarbene complexes in general. This had become apparent already from the structural data of many zirconoxycarbene complexes, featuring much shorter O–C(carbene) distances than typically observed for carbene complexes of the Fischer type.[1] For a wide use of our novel approach to (metaloxy)carbene complexes in organometallic and organic synthesis it was, therefore, necessary to develop ways of converting complexes like **2** or **3** into conventional heteratom-stabilized carbene complexes $(CO)_5M{=}CR(OR')$.

We here report several examples showing that this can easily be achieved by a simple hydrolytic replacement of the early transition metal from the metallacyclic zirconoxycarbene complex system.

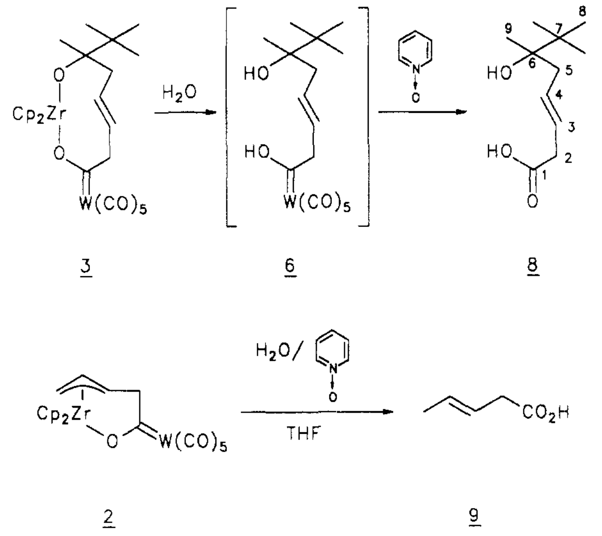
Results and Discussion

The zirconoxycarbene complexes **2** or **3** can be converted to metal-free organic products by a combination of reactions involving hydrolytic removal of the early transition metal and conventional transformations of Fischer-type carbene complexes. We have thus added 2 mol equiv of water to a solution of the metallacycle **3** in tetrahydrofuran, followed by ca. 2.5 equiv of diazomethane in ether.[6] After a period of ca. 3 h no residual starting material was detected by IR spectroscopy. From the solution a 85:15 mixture of the methoxydienol isomers **4a** and **4b** was isolated in 90% yield (Scheme II).

Scheme III



Scheme IV



The reaction of the (π-allyl)zirconoxycarbene complex **2** with H_2O/diazomethane proceeds similarly. *trans*-2-Methoxy-1,4-hexadiene [**5**: ^{13}C NMR (C_6) δ 17.9; IR ν 969 cm^{-1}] was isolated in ca. 30% yield. It was the only organic product obtained. Hydrolysis of the carbene complex **3** in the absence of an additional trapping reagent (like diazomethane) takes a somewhat different course. In this case, the reaction is less clean. The major reaction pathway taken involves carbon–carbon bond cleavage, giving hexacarbonyltungsten and a 45:55 mixture of the alcohols **7a** and **7b**[7] (Scheme III). Apparently, the hydroxycarbene complex **6**, serving as an intermediate in the hydrolysis reaction, is not stable under the reaction conditions applied but rather rapidly decomposes by metal carbonyl formation.[8]

The hydroxycarbene complex intermediate **6** can be trapped by oxidizing reagents as well.[9] We have hydrolyzed the zirconoxycarbene complex **3** in tetrahydrofuran at ambient temperature in the presence of pyridine *N*-oxide and isolated *trans*-6-hydroxy-6,7,7-trimethyl-3-octenoic acid (**8**) in >50% yield. Analogous treatment of the carbene complex **2** with H_2O/pyridine *N*-oxide yielded *trans*-3-pentenoic acid (**9**, Scheme IV).

The reactions described above show that metallacyclic zirconoxycarbene complexes can hydrolytically be converted into zirconium-free hydroxycarbene metal complexes quite easily. However, the use of this type of a primary product (e.g., **6**) seems to be limited due to a rather rapidly proceeding subsequent C–C bond cleavage

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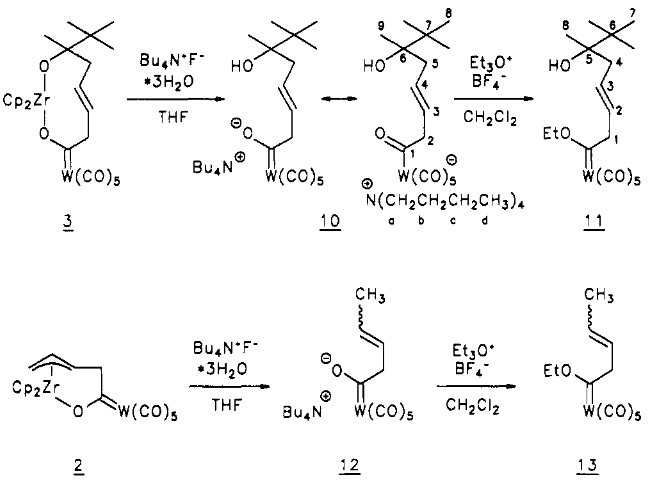
Scheme V



liberating the metal carbonyl (here $W(CO)_6$). Only in the presence of reactive scavengers (here CH_2N_2 or C_5H_5NO) does the rapid metal carbonyl producing fragmentation reaction not represent a severe limitation for using the hydrolytic cleavage of zirconoxycarbene complexes synthetically. For the preparation of conventional Fischer-type carbene complexes the overall procedure had to be altered leading to acylmetallate anions as reactive intermediates rather than the neutral hydroxycarbene transition-metal complexes. This was achieved by using tetra-*n*-butylammonium fluoride trihydrate instead of stoichiometric amounts of water in the "hydrolysis" step.

We have reacted the zirconoxycarbene complex **3** with 1 mol equiv of $Bu_4N^+F^-\cdot 3H_2O$ in tetrahydrofuran at 0 °C. From the reaction mixture the tetra-*n*-butylammonium acylmetallate **10** was isolated in 80% yield (IR ν(CO) 2041, 1942, 1897, 1878 cm^{-1}). A ^{1}H NMR ^3J(H3,H4) coupling constant of 15.4 Hz indicated the presence of a *trans*-C=C double bond. Complex **10** exhibited a ^{1}H NMR OH resonance at δ 3.13 (exchanged with D_2O). Addition of triethyloxonium tetrafluoroborate (Meerwein's reagent) in methylene chloride cleanly converted **10** into the neutral Fischer carbene complex **11**[10] (Scheme V; >90% yield; IR ν(CO) 2071, 1955, 1945 cm^{-1}).

Quite similarly, the zirconoxycarbene complex **2** was converted to an acylmetallate anion system (**12**) by treatment with $Bu_4N^+F^-\cdot 3H_2O$ in tetrahydrofuran. Only in this case we have obtained a mixture of cis/trans isomers (70% yield). Addition of Meerwein's reagent produced the neutral tungsten carbene complex **13** (ca. 50% isolated, two isomers in a 40:60 ratio).

We have shown that the addition of various (η^2-olefin)metallocene type reagents (e.g., (butadiene)$ZrCp_2$, (butadiene)$HfCp_2$, (butadiene)$ThCp^*_2$, (aryne)$TiCp_2$, (aryne)$ZrCp_2$, (η^2-formaldehyde)$ZrCp_2$, etc.) to metal carbonyls can very effectively be used to prepare many (metaloxy)carbene complexes (e.g., of Zr, Hf, V, Nb, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ni, Pt).[1] This essentially nonnucleophilic carbene synthesis very nicely complements the conventional (nucleophilic) variations of E. O. Fischer's original carbene complex synthesis[2,10] that have been developed so far. The hydrolytic conversion of the quite unreactive (metaloxy)carbene complexes leading directly to metal-free organic products or to ordinary Fischer carbene complexes, as described for the selected examples in this article, will probably extend the use of our novel method of a carbene complex synthesis considerably. Preliminary experiments have already revealed that the procedures described here can readily be applied to prepare Fischer-type carbene complexes that were believed not to be available from metal carbonyls by the conventional methods.

Experimental Section

Reactions with organometallic compounds were carried out in an argon atmosphere using Schlenk type glassware. Solvents were freshly distilled from potassium/benzophenone (THF), lithium aluminum hydride (diethyl ether, *n*-hexane), or P_4O_{10} (methylene chloride) prior to use. Benzene-d_6 and THF-d_8 were dried over sodium/potassium alloy and $CDCl_3$ over P_4O_{10} (Sicapent, Merck) and subsequently distilled. Pyridine *N*-oxide was sublimed in vacuo. Stock solutions of pyridine *N*-oxide and tetrabutylammonium fluoride trihydrate with known concentrations were prepared and used in the reactions. The following spectrometers were used: NMR, Bruker WP 200 SY (^{1}H 200.1 MHz, ^{13}C 50.3 MHz), ^{1}H chemical shifts given with multiplicity, integral, and assignment in parentheses, ^{13}C NMR data give ^1J(C,H) coupling constants in parentheses; IR, Nicolet 5DXC FT IR spectrometer; MS, Varian MAT CH7 and Finnigan 8200 MAT (GC MS, exact mass). Elemental analyses were carried out at the Mikroanalytisches Laboratorium des Instituts für Anorganische Chemie der Universität Würzburg. Melting points are uncorrected. Complexes **1**,[11] **2**,[3] and **3**[4] were prepared according to literature procedures. All reactions were monitored by IR to ensure complete consumption of starting materials.

***trans*-8-Methoxy-2,2,3-trimethylnona-5,8-dien-3-ol (4a) and 8-Methoxy-2,2,3-trimethylnona-6,8-dien-3-ol (4b).** To a solution of 670 mg (0.92 mmol) of **3** in 10 mL of THF was added 0.035 mL (1.9 mmol) of water. Then, 4.0 mL of a 0.26 M solution of diazomethane in diethyl ether[12] (1.04 mmol) was added dropwise at room temperature (for larger scale reactions ice cooling is required) with occasional shaking. The yellow mixture turned orange. After 1 h another 4.0-mL portion of etheral diazomethane solution was added. After 1 h air was bubbled through the solution (5 min), and the mixture was allowed to stand overnight. The mixture was filtered, and the filtrate evaporated to dryness. The dark oily residue was redissolved in 6 mL of methanol, and the solution decanted from a remaining precipitate. The solvent was evaporated, and the residue dried in vacuo to give 180 mg (92%) of **4a** and **4b** (85:15 mixture by ^{1}H NMR) as a brownish oil. ^{1}H NMR (C_6D_6): **4a**, δ 5.70–5.44 (m, 2 H, H6 and H5), 3.95 (d, 1 H, H9$_{cis}$), 3.84 (d, 1 H, H9$_{trans}$), 3.21 (s, 3 H, OCH_3), 2.91–2.79 (m, 2 H, H7), 2.22 (m, 1 H, H4′), 1.98 (m, 1 H, H4), 1.17 (s, 1 H, OH), 1.00 (d, 3 H, H10), 0.92 (s, 9 H, H1), coupling constants (Hz) ^2J = 1.9 (H9$_{cis}$, H9$_{trans}$), ^4J = 0.9 (H4 or H4′, H10); **4b**, δ 3.98 (d, H9$_{cis}$), 3.90 (d, H9$_{trans}$), 3.08 (s, OCH_3, 1.75–1.47 (m, H4 and H5), 1.26 (s, OH), 1.02 (d, H10), 0.93 (s, H1) (the other signals of **4b** are probably hidden under the signals of **4a** or were too weak to be localized) coupling constants (Hz) ^2J = 1.8 (H9$_{cis}$, H9$_{trans}$), ^4J = 0.8 (H4 or H4′, H10). ^{13}C NMR (C_6D_6): **4a**, δ 163.6 (C8), 129.9, 129.4 (C5,C6), 80.8 (C9), 76.1 (C3), 58.2 (OCH_3), 40.0 (C7), 38.7 (C4), 38.0 (C2), 25.6 (C1), 21.6 (C10); **4b**, δ 162.7 (C8), 130.0 (C5 or C6), 81.3 (C9) (the remaining signals of **4b** were not localized). IR (cyclohexane, mixture of isomers) 3631, 3582, 1655, 1598, 976, 800 cm^{-1}. MS (EI), 212 ($M^{+\bullet}$, 0.2), 101 (100). Exact mass (CI) calcd for $C_{13}H_{24}O_2$ 212.1776 ($M^{+\bullet}$), found 212.1782.

***trans*-2-Methoxy-1,4-hexadiene (5).** A solution of 2.77 g (4.41 mmol) of **2** in 25 mL of THF was cooled to 0 °C, and 0.16 mL (8.9 mmol) of water was added. Then 37.0 mL of a 0.25 M solution of diazomethane in diethyl ether (9.25 mmol) was added dropwise over 10 min with occasional shaking of the reaction tube. The yellow solution turned orange. The mixture was kept at 0 °C for 4 h. Argon was then bubbled through the solution, and the mixture was allowed to stand overnight. The reaction mixture was filtered, and all volatiles were condensed at liquid nitrogen temperature. Most of the solvent was distilled from the con-

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[12] *Organikum*; VEB Deutscher Verlag der Wissenschaften: Berlin, 1981; p 672.

densate through a 20-cm Vigreux column. The residue was fractionized by Kugelrohr distillation. The fractions between 90 and 120 °C afforded 299 mg of a colorless liquid, which contained approximately 1.2 mmol (27%) of diene **5** and some THF (by ^{1}H NMR). ^{1}H NMR (C_6D_6) δ 5.68–5.30 (m, 2 H, H4 and H5), 3.96 (d, 1 H, $H1_{cis}$), 3.84 (d, 1 H, $H1_{trans}$), 3.21 (s, 3 H, OCH_3), 2.85 (br d, 2 H, H3), 1.54 (dq, 3 H, H6), coupling constants (Hz) ^2J = 1.9 ($H1_{cis}/H1_{trans}$), ^3J = 6.0 (H5, H6), ^4J = 1.3 (H4, H6), ^5J = 1.3 (H3, H6). ^{13}C NMR (C_6D_6) δ 163.8 (C2), 127.8, (C5, 147), 127.1 (C4, 152), 80.6 (Cl, 158), 54.4 (OCH_3, 143), 38.7 (C3, 128), 17.9 (C6, 126). IR (NaCl) 1646, 1605, 969, 800 cm^{-1}, GC MS (EI, SE 30, 30 m, 50 °C), 112 ($M^{+\bullet}$, 100). Exact mass (GC MS, EI) calcd for $C_7H_{12}O$ 112.0888 ($M^{+\bullet}$), found 112.0890.

Reaction of the Zirconoxycarbene Complex 3 with Water. To a solution of 90 mg (0.12 mmol) of the carbene complex **3** in 0.5 mL of tetrahydrofuran-d_8 water (2.5 μL, 0.14 mmol) was added. The progress of the hydrolysis reaction was followed by ^{1}H NMR spectroscopy. The product 2,2,3-trimethylhept-6-en-3-ol (**7b**) could be detected after 10 min at ambient temperature; ca. 50% transformation had been achieved after 3 h. After 6 h of reaction time an additional 2.5 μL (0.14 mmol) of water was added, and the mixture allowed to react overnight. After 24 h complex **3** was completely hydrolyzed. The ^{1}H NMR spectrum showed the signals of 2,2,3-trimethylhept-5-en-3-ol (**7a**) and 2,2,3-trimethylhept-6-en-3-ol (**7b**) in a 45:55 ratio (identified by comparison with authentic material[7]) plus free cyclopentadiene and some $(Cp_2ZrO)_3$ (δ 6.31, Cp). Hexacarbonyltungsten was identified by ^{13}C NMR and IR spectroscopy.

***trans*-6-Hydroxy-6,7,7-trimethyl-3-octenoic acid (8).** A solution of 2.35 g (3.23 mmol) of **3** in 50 mL of THF was treated with 370 mg (3.90 mmol) of pyridine *N*-oxide (5.7 mL of a THF solution) and 0.12 mL (6.67 mmol) water. After 3.5 h the solvent was removed in vacuo, and the residue redissolved in 40 mL of diethyl ether. Water (20 mL) was added, and the mixture was acidified with 4 M hydrochloric acid. The yellow organic phase was separated. The water phase was extracted four times with 20-mL portions of diethyl ether. The combined organic phases were washed with brine, filtered, and dried over sodium sulfate. The solvent was evaporated to give 1.52 g of an viscous residue, which was redissolved in 30 mL of diethyl ether. The solution was extracted three times with 20-mL portions of saturated sodium hydrogen carbonate solution. The combined extracts were treated with 4 M hydrochloric acid until ca. pH 3 was reached. The cloudy mixture was extracted five times with 20-mL portions of diethyl ether. The combined organic phases were washed with brine, dried over sodium sulfate, filtered, and evaporated to dryness to give 361 mg (55%) of **8** as a pale yellow oil. Anal. Calcd for $C_{11}H_{20}O_3$ (200.3): C, 65.97; H, 10.07. Found: C, 65.52; H, 10.38. ^{1}H NMR ($CDCl_3$) δ 5.72 (dt, 1 H, H4), 5.57 (dt, 1 H, H3), 5.1 (br, 2 H, OH and CO_2H), 3.10 (d, 2 H, H2), 2.33 (dd, 1 H, H5′), 2.16 (dd, 1 H, H5), 1.09 (s, 3 H, H9), 0.93 (s, 9 H, H8), coupling constants (Hz) ^2J = 13.8 (H5, H5′), ^3J = 6.2 (H2, H3), 15.5 (H3, H4) 6.7 (H4, H5) 6.7 (H4, H5′). ^{13}C NMR ($CDCl_3$) δ 177.0 (C1), 131.1 (C4), 125.0 (C3), 76.5 (C6), 39.3 (C2), 37.8 (C5), 37.7 (C7), 25.2 (C8), 21.4 (C9). IR (NaCl) 3440, 1714, 974 cm^{-1}. MS (EI) 143 (10), 101 (96), 43 (100).

***trans*-3-Pentenoic Acid (9).** To a solution of 3.13 g (4.99 mmol) of **2** in 80 mL of THF were added 475 mg (4.99 mmol) of pyridine *N*-oxide in 7.3 mL of THF and 0.20 mL (11.1 mmol) of water. The yellow solution turned orange and warmed up a little. After 2 h the reaction mixture was concentrated by using a rotary evaporator. To the dark oily residue was added 50 mL of diethyl ether, and the resulting solution was extracted five times with 50-mL portions of satured sodium carbonate solution. The combined extracts were washed twice with diethyl ether, acidified with 5 M hydrochloric acid (pH 2–3), saturated with sodium chloride, and extracted with 80 mL of diethyl ether. The water phase was extracted four additional times with 40-mL portions of diethyl ether. The combined organic phases were washed twice with brine, dried over sodium sulfate, and concentrated. The brownish residue was dried in vacuo (25 mbar, 10 min). Trap-to-trap distillation gave 80 mg (16%) of **9** as a colorless liquid. Anal. Calcd for $C_5H_8O_2$ (100.1): C, 59.98; H, 8.05. Found: C, 58.36; H, 7.85. ^{1}H NMR (C_6D_6) δ 11 (br, 1 H, CO_2H), 5.62–5.10 (m, 2 H, H3 and H4), 2.73 (d quintet, 2 H, H2), 1.42 (dq, 3 H, H5), coupling constants (Hz) ^3J = 6.6 (H2, H3) 6.1 (H4, H5), ^4J = 1.3 (H2, H4) 1.3 (H3, H5), ^5J = 1.3 (H2, H5). ^{13}C NMR (C_6D_6) δ 179.0 (C1), 129.2 (C4), 122.7 (C3), 37.9 (C2), 17.8 (C5). IR (NaCl) 3600–2300 (br), 1711, 966 cm^{-1}. MS (EI), 100 ($M^{+\bullet}$, 41), 55 (100).

Tetrabutylammonium [1-η-*trans*-6-Hydroxy-6,7,7-trimethyl-1-oxo-3-octen-1-yl]pentacarbonyltungstate(0) (10). To a sample of 870 mg (1.20 mmol) of **3** in 50 mL of THF was added 3.72 mL of a THF solution containing 378 mg (1.20 mmol) tetrabutylammonium fluoride trihydrate at 0 °C over 20 min. The mixture was stirred at 0 °C for 2 h to decompose trimeric zirconocene oxide. The mixture was stirred at 0 °C for 2 h to decompose trimeric zirconocene oxide. The solvent was then removed in vacuo. The residue was extracted with 50 mL of diethyl ether and filtered. The solvent was evaporated, and the residue dried in vacuo to give 720 mg (80%) of **10** as a yellow oil. Anal. Calcd for $C_{32}H_{55}NO_7W$ (749.6): C, 51.27; H, 7.40; N, 1.87. Found: C, 51.12; H, 7.43; N, 1.78. ^{1}H NMR (C_6D_6) δ 5.64 (ddd, 1 H, H4), 5.41 (ddd, 1 H, H3), 4.12 (dd, 1 H, H2′), 3.72 (dd, 1 H, H2), 3.13 (s, 1 H, OH), 2.88 (m, 8 H, H-a), 2.25 (dd, 1 H, H5′), 2.12 (dd, 1 H, H5), 1.49–1.15 (m, 16 H, H-b and H-c), 1.08 (s, 3 H, H9), 1.02 (s, 9 H, H8), 0.96 (t, 12 H, H-d), coupling constants (Hz) ^2J = 15.7 (H2, H2′), 12.7 (H5, H5′), ^3J = 8.7 (H2, H3) 5.6 (H2′, H3), 15.4 (H3, H4) 5.7 (H4, H5) 8.9 (H4, H5′). ^{13}C NMR (C_6D_6) δ 276.4 (C1, ^1J(W,C) = 80 Hz), 209.3 (C–CO_{trans}, ^1J(W,C) = 138 Hz), 204.9 (C–CO_{cis}, ^1J(W,C) = 127 Hz), 133.5 (C4, 153), 127.5 (C3, 152; in $CDCl_3$ δ 126.8), 74.8 (C2, 126), 74.5 (C6), 58.6 (C-a, 143), 40.0 (C5, 127), 37.6 (C7), 25.8 (C8, 123), 23.9 (C-b, 127), 22.6 (C9, 126), 19.9 (C-c, 122), 13.8 (C-d, 121). IR (THF) 2041, 1942, 1897, 1878 (sh) cm^{-1}. MS (EI), 185 (0.9), 142 (19), 43 (100).

Pentacarbonyl[ethoxy(*trans*-5-hydroxy-5,6,6-trimethyl-2-hepten-1-yl)carbene]tungsten (11). The ammonium salt **10** (340 mg, 0.45 mmol) was dissolved in 50 mL of methylene chloride, cooled to 0 °C, and treated with 0.47 mL of a 1 M methylene chloride solution of triethyloxonium tetrafluoroborate (0.47 mmol). After 1 h of stirring at 0 °C the solvent was removed in vacuo. The residue was stirred for 1 h with 30 mL of *n*-hexane and filtered. The filtrate was concentrated and cooled to −30 °C to precipitate most of the $W(CO)_6$. The solution was decanted and evaporated to dryness, affording 220 mg (91%) of **11** as an orange, very viscous oil. ^{1}H NMR ($CDCl_3$) δ 5.49 (br dt, 1 H, H3), 5.40 (br dt, 1 H, H2), 4.86 (q, 2 H, OCH_2CH_3), 3.89 (d, 2 H, H1), 2.30 (br dd, 1 H, H4′), 2.12 (br dd, 1 H, H4), 1.58 (t, 3 H, OCH_2CH_3), 1.25 (br, 1 H, OH), 1.07 (d, 3 H, H8), 0.93 (s, 9 H, H7), coupling constants (Hz) ^2J = 13.8 (H4, H4′), ^3J = 6.9 (H1, H2), 15.4 (H2, H3), 7.6 (H3, H4) 7.0 (H3, H4′) 7.1 (OCH_2CH_3), ^4J = 0.8 (H4 or H4′, H8). ^{13}C NMR ($CDCl_3$) δ 329.7 (C-carbene, ^1J(W,C) = 104 Hz, 203.1 (C–CO_{trans}), 197.2 (C–CO_{cis}, ^1J(W,C) = 127 Hz), 131.8 (C3, 155), 126.0 (C2, 159), 80.6 (OCH_2CH_3, 149), 75.8 (C5, in C_6D_6 δ 75.5), 68.1 (C1, 129), 39.7 (C4, 125), 37.8 (C6), 25.3 (C7, 130), 21.7 (C8, 126), 14.7 (OCH_2CH_3, 127). IR (*n*-hexane) 2071, 1955, 1945 cm^{-1}. MS (EI), 536 ($M^{+\bullet}$, 0.3), 43 (100). Exact mass (EI) calcd for $C_{18}H_{24}O_7W$ 534.1005 ($M^{+\bullet}(^{182}W)$), found 534.1012.

Tetrabutylammonium [1-η-1-Oxo-3-penten-1-yl]pentacarbonyltungstate(0) (12). To a solution of 790 mg (1.26 mmol) of **2** in 50 mL of THF was added at 0 °C 3.91 mL of a THF solution containing 397 mg (1.26 mmol) of tetrabutylammonium fluoride trihydrate. The mixture was stirred at 0 °C for 2 h. The solvent was removed in vacuo, and the residue stirred for 2 h with 50 mL of diethyl ether. The mixture was filtered, the solvent was evaporated, and the residue dried in vacuo to give 590 mg (72%) of **12** as an orange oil, which crystallized after several hours, mp 50 °C. The ^{1}H NMR spectrum revealed a 35:65 mixture of cis and trans isomer. Anal. Calcd for $C_{26}H_{43}NO_6W$ (649.5): C, 48.08; H, 6.67; N, 2.16. Found: C, 47.90; H, 6.93; N, 2.10. ^{1}H NMR (C_6D_6/THF-d_8 10:1, mixture of isomers) δ 6.05–5.78 (m, 1 H, H4(c,t)), 5.70–5.44 (m, 1 H, H3(c,t)), 3.82 (br d, H2(c)), 3.70 (br d, H2(t); together with H2(c), 2 H), 2.88 (m, 8 H, H-a), 1.72 (br d, 3 H, H5(c,t)), 1.45–1.09 (m, 16 H, H-b and H-c), 0.93 (t, 12 H, H-d), coupling constants (Hz) ^3J = 7.1 (H2, H3(t)) 6.7 (H2, H3(c)) 6.3 (H4, H5). ^{13}C NMR (THF-d_8), *trans*-**12** δ 275.6 (C1), 208.8 (C–CO_{trans}), 205.2 (C-CO_{cis}, ^1J(W,C) = 128 Hz), 129.6 (C4, 154), 125.0 (C3, 148), 74.6 (C2, 126), 59.3 (C-a, 143), 24.6 (C-b, 125), 20.5 (C-c, 122), 18.5 (C5, 125), 13.9 (C-d, 125); *cis*-**12** δ 274.1 (C1), 128.3, (C4, 155), 122.5 (C3, 152), 69.0 (C2, 124), 13.5 (C1) (the remaining signals of *cis*-**12** were not localized). IR (THF, mixture of isomers) 2040, 1942, 1898, 1875 cm^{-1}. MS (EI), 185 (2.9), 41 (100).

Pentacarbonyl[ethoxy(2-buten-1-yl)carbene]tungsten (13). A solution of 1.23 g (1.89 mmol) of **12** in 100 mL methylene chloride was treated at 0 °C with 2.0 mL of a 1 M methylene chloride solution of triethyloxonium tetrafluoroborate over 10 min. The mixture was stirred for additional 0.5 h at 0 °C. The solvent was removed in vacuo, and the residue stirred for 1 h in 100 mL of *n*-hexane. A precipitate was filtered off, and the solution concentrated to one-quarter volume. $W(CO)_6$ was filtered off, and the solution was cooled to −30 °C to crystallize residual $W(CO)_6$. The solution was decanted, and the solvent evaporated. The residue was dried in vacuo (0.5 h) to give 400 mg (49%) **13** as a red brown oil. ^1H NMR spectroscopy revealed a 40:60 mixture of cis and trans isomer. Anal. Calcd for $C_{12}H_{12}O_6W$ (436.1): C 33.05, H 2.77. Found: C 33.29, H, 2.66. ^1H NMR (C_6D_6, mixture of isomers) δ 5.56–5.10 (m, 2 H, H2 and H3 of cis and trans isomer), 4.36 (q, 2 H, OCH_2CH_3 of cis and trans isomer), 3.67 (br d, H1(c)), 3.55 (br d, H1(t); together with H1(c), 2 H), 1.47 (dq, H4(t)), 1.43 (ddt, H4(c); together with H4(t), 3 H), 0.94 (t OCH_2CH_3(t)), 0.92 (t, OCH_2CH_3(c); together with trans isomer, 3 H), coupling constants (Hz), *trans*-**13**, ^3J = 6.7 (H1, H2) 6.1 (H3, H4) 7.1 (OCH_2CH_3), ^4J = 1.2 (H2, H4), ^5J = 0.9 (H1, H4), *cis*-**13**, ^3J = 7.0 (H1, H2) 6.7 (H3, H4) 7.1 (OCH_2CH_3), ^4J = 1.7 (H2, H4), ^5J = 0.9 (H1, H4). ^{13}C NMR (C_6D_6, mixture of isomers) δ 330.4, 330.3 (C–carbene(c,t)), 203.3 (C–CO_{trans}(c,t)), 197.6 (C–CO_{cis}(c,t)), 130.4 (C3(t), 153), 127.7 (C3(c), 149), 123.7 (C2(t), 158), 122.6 (C2(c), 159), 80.6 (OCH_2CH_3(c,t), 149), 68.1 (C1(t), 128), 62.9 (C1(c), 129), 17.9 (C4(t), 120) 14.1 (OCH_2CH_3(c,t), 127), 13.2 (C4(c), 127), the resonances of the ethoxy group and the metal carbonyl carbons were not resolved. IR (NaCl, mixture of isomers) 2070, 1978 (sh), 1936 (v strong) cm^{-1}. MS (EI), 436 ($M^{+\bullet}$, 28), 323 (100), 295 (81), 268 (49).

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Mechanistic Aspects of the Cyclometalation of Quinoline-8-carboxaldehyde with Platinum(II)

Clemens G. Anklin

Spectrospin AG, CH-8117 Fällanden, Switzerland

Paul S. Pregosin,* Franz J. Wombacher, and Hubert J. Rüegg

Laboratorium für Anorganische Chemie, ETH-Z, CH-8092 Zürich, Switzerland

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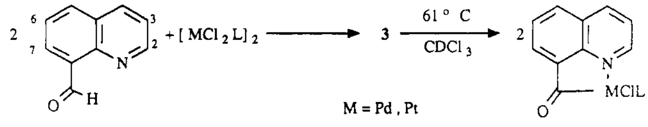
Rates of reaction at 61 °C in $CDCl_3$ for the cyclometalation of quinoline-8-carboxaldehyde (1) with *trans*-$PtCl_2(1)L$ (L = PEt_3, PBu^n_3, PPh_3, $PTol_3$, $AsEt_3$, $AsPr^i_3$, $AsTol_3$) are reported. Starting from *trans*-$PtCl_2(1)(PEt_3)$, there is a kinetic isotope effect k_H/k_D = 1.4. Modification of the Pt(II) complex to *trans*-$PtBr_2(1)L$ enhances the rate by a factor of ca. 70. The use of *sym-trans*-$[Pt(\mu\text{-}Cl)(SnCl_3)(PTol_3)]_2$ and 2 equiv of 1 affords facile cyclometalation at room temperature within the mixing time. The direct generation of cationic complexes via *cis*-$PtCl_2L_2$ plus $Ag(CF_3SO_3)$ followed by addition of 1 is also shown to lead to facile cyclometalation. All of these reactions are discussed in terms of the importance of cationic metal compounds. Synthetically, the most efficient cyclometalation of 1 can be accomplished by using $[Pt(\mu\text{-}Cl)(\eta^3\text{-}CH_2C(CH_3)CH_2)]_2$. ^1H and ^{31}P NMR data are given for selected examples.

Introduction

The cyclometalation reaction is now a well-known synthetic method for creating metal–carbon bonds.[1] Despite this, there are not many studies concerned with its mechanistic detail[2] and most of these are related to palladium chemistry.[3] We have been involved in the cyclometalation of various aldehyde ligands[4a] and have observed a facile metalation of quinoline-8-carboxaldehyde (**1**) using both Pd(II) and Pt(II).[4b] The chemistry of eq 1 contains at least two well-defined steps, as do many cyclometalations,[1] the first of which involves the room-temperature reaction of the dimer with 2 equiv of **1** to afford *trans*-$MCl_2(1)L$ (**3**, which has an interesting M–H–C interaction[5,6]) and subsequent cyclometalation at 61 °C in chloroform.



1 **2** **4**

M = Pt, L = PEt_3 (**4a**), $PTol_3$ (**4b**), PPh_3 (**4c**), $AsEt_3$ (**4d**), $AsTol_3$ (**4e**), $AsPr^i_3$ (**4f**)

(1)

Despite the relative ease of this reaction and the known[7] oxidative addition of **1** to Rh(I), it is not certain which

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