Electrophilic Benzylidene(pentacarbonyl)-chromium(0) and -tungsten(0) Complexes: Isolation, Characterization, and an Unusual Thermolytic Reaction of the Tungsten Compounds

Helmut Fischer,* Siegfried Zeuner, and Klaus Ackermann

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-8046 Garching, West Germany

The reaction of the anionic alkyl complexes of chromium and tungsten, $NEt_4^+[(CO)_5M\{CH(OMe)(p\text{-}C_6H_4R)\}]^-$ (M = Cr, R = OMe; M = W, R = OMe, Me, H) with $HBF_4 \cdot Et_2O$ yields isolable, strongly electrophilic benzylidene(pentacarbonyl) complexes, $(CO)_5M{=}CH(p\text{-}C_6H_4R)$; thermolysis of the tungsten compounds gives μ-benzylidenebis(pentacarbonyltungsten) complexes, $[(CO)_5W]_2[\mu\text{-}CH(p\text{-}C_6H_4R)]$.

Alkylidene(pentacarbonyl) complexes (monoaryl- and monoalkyl-carbene complexes) of chromium(0) and tungsten(0) are expected to be particularly interesting compounds for the following reasons. (i) Since alkylidene complexes of W^{II}, W^{IV}, and W^{VI} are known, complexes of W^0 should offer the opportunity to compare the influence of different oxidation states of the metal on the properties and the reactivity of the alkylidene ligand. (ii) Carbene complexes are known as metathesis catalysts. A carbene complex with two non-metal substituents of significantly different size therefore allows the study of steric influences on the course of the metathesis reaction. (iii) Because of the high electrophilicity of the alkylidene carbon atom, these compounds should function as high yield 'CH(R)' sources towards nucleophilic substrates under very mild conditions.

However, benzylidene(pentacarbonyl)tungsten could only be generated at −78 °C in an earlier report and was identified by its ^1H n.m.r. spectrum and by some trapping reactions.[1]

Herein we report the synthesis, first isolation, and characterization of several benzylidene complexes of chromium(0) and tungsten(0), and the thermally induced dimerization of the tungsten compounds. The last reaction proceeds with elimination of one benzylidene ligand to give μ-benzylidenebis(pentacarbonyltungsten) complexes.

When $NEt_4^+[(CO)_5M\{CH(OMe)(p\text{-}C_6H_4R)\}]^-$ complexes (**1a**—**d**), synthesized in high yield from $(CO)_5M[C(OMe)(p\text{-}C_6H_4R)]$ and $[HB(OPr^i)_3]^-$,[1,2] were each treated in dichloromethane at −78 °C with three equivalents of $HBF_4{\cdot}Et_2O$, the original yellow solutions turned dark red and $(CO)_5M{=}CH(p\text{-}C_6H_4R)$ (**2a**—**d**) were formed almost quantitatively [reaction (1)].

$$\underset{\textbf{(1a—d)}}{[(CO)_5M\{CH(OMe)(p\text{-}C_6H_4R)\}]^-} + HBF_4{\cdot}Et_2O \longrightarrow$$

$$\underset{\textbf{(2a—d)}}{(CO)_5M{=}CH(p\text{-}C_6H_4R)} + MeOH + BF_4^- + Et_2O \qquad (1)$$

a; M = W, R = OMe
b; M = W, R = Me
c; M = W, R = H
d; M = Cr, R = OMe

Immediate purification of (**2a**—**d**) by column chromatography at −70 °C followed by recrystallization gave compounds (**2a**—**d**) in 50—80% yield in the form of dark-red, almost black crystals. The compounds (**2a**—**d**) were characterized by elemental analysis (C, H, O, W, and Cr) and by spectroscopic methods.[†] The i.r. spectra show that the benzylidene ligand in (**2a**—**d**) exhibits only a slightly smaller σ-donor/π-acceptor ratio than '$C(p\text{-}C_6H_4R)Ph$' in aryl(phenyl)carbene complexes.[3] The benzylidene hydrogen is strongly deshielded whereas the benzylidene carbon signal is found in the range characteristic for non-heteroatom stabilized carbene complexes.

The thermal stabilities of (**2a**—**d**) are strongly influenced by their purity and vary markedly with the substituent R. Pure (**2c**) decomposes at 20 °C in CH_2Cl_2 solution with a half-life of *ca.* 2 min; (**2a**), however, can be handled at room temperature for short periods of time and (**2d**) is comparable in stability to (**2c**). As expected, (**2d**) decomposes to give $(CO)_6Cr$ as the main product. In contrast, the tungsten compounds (**2a**—**c**) on thermolysis in hexane, CH_2Cl_2, or in the solid state react in a novel and surprising way, one which so far has not been observed with carbene complexes. Dimerization and elimination of one benzylidene ligand gave red-brown μ-benzylidenebis(pentacarbonyltungsten) complexes (**3a**—**c**), *cis*- and *trans*-stilbenes [*e.g. cis* : *trans* 1 : 3.6 for (**2c**)], and the corresponding *para*-substituted toluene [reaction (2)].

$$\underset{\textbf{(2a—c)}}{2(CO)_5W{=}CH(p\text{-}C_6H_4R)} \longrightarrow \underset{\textbf{(3a—c)}}{[(CO)_5W]_2[\mu\text{-}CH(p\text{-}C_6H_4R)]} +$$

$$1/2\,(p\text{-}C_6H_4R)HC{=}CH(p\text{-}C_6H_4R) + MeC_6H_4R + \ldots \qquad (2)$$

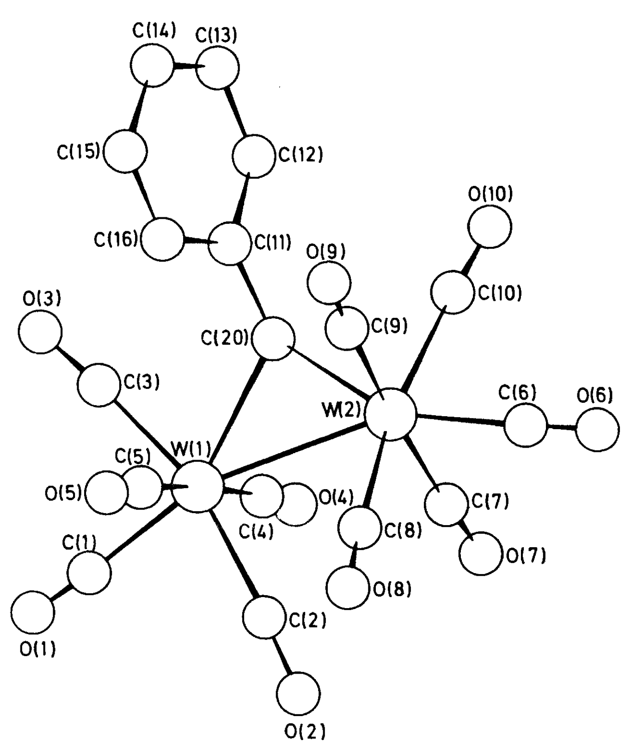

Figure 1. Molecular structure of $[(CO)_5W]_2[\mu\text{-}CH(Ph)]$ (**3c**). Some important distances (pm) and angles (°) are (e.s.d.s in parentheses): W(1)–W(2) 311.8(1), W(1)–C(20) 226.5(8), W(2)–C(20) 229.0(8), C(20)–W(1)–W(2) 47.1(2); C(20)–W(2)–W(1) 46.5(2); angle between plane 1 [C(2)C(3)C(4)C(5)] and plane 2 [C(7)C(8)C(9)C(10)] 42°.

A similar type of thermolysis reaction has been found only with some allenylidene(pentacarbonyl) complexes.[4] In a succeeding step, (**3a**—**c**) decompose slowly, initiated by loss of a CO ligand. The dimeric complexes (**3**) (isolated: 30—55%) were characterized spectroscopically,[‡] by elemental analysis, and, in the case of (**3c**), by an *X*-ray structure determination (Figure 1).[§] The thermolysis reaction is autocatalytic. In the initial reaction period the rate [*e.g.*, k for (**2a**) = 2.3×10^{-3} s^{-1} at 47.5 °C] is independent of the concentration of (**2a**—**c**). The formation of (**3a**—**c**) can be regarded as the addition of a $(CO)_5W$ fragment to the W=C(benzylidene) double bond. Consequently, (**2a**) reacts rapidly in CH_2Cl_2 at 0 °C with $(CO)_5W(CH_2Cl_2)$ [prepared photochemically *in situ* from $(CO)_6W$ and CH_2Cl_2] to give (**3a**). When the same conditions are applied to pure (**2a**) in CH_2Cl_2, the formation of (**3a**) is at least 20 times slower. The addition of an *electrophilic* ligand–metal fragment to the M=C(carbene) bond of carbene

---

[†] Selected spectroscopic data: ν_{CO} (hexane) (**2a**), 2068s, 1962vs; (**2b**), 2074s, 1969vs; (**2c**), 2076s, 1973vs; (**2d**), 2062s, 1977vs, 1967vs cm^{-1}. N.m.r., ^1H (CD_2Cl_2, −70 °C, rel. to $CDHCl_2$) δ (**2a**), 16.18; (**2b**), 16.74; (**2c**), 17.53; (**2d**), 16.45 (all benzylidene C-*H*); ^{13}C (CD_2Cl_2, −70 °C, rel. to CD_2Cl_2) δ (**2a**), 327.0 (J_{CH} 120.8 Hz); (**2b**), 334.9 (J_{CH} 120.8 Hz); (**2c**), 338.7 (J_{CH} 123.3 Hz); (**2d**), 364.8 (J_{CH} 127.0 Hz) (all benzylidene *C*–H).

[‡] Selected spectroscopic data: n.m.r., ^1H (CD_2Cl_2, −70 °C, rel. to $CDHCl_2$) δ (**3a**), 10.50; (**3b**), 10.38; (**3c**), 10.27 (all benzylidene μ-C-*H*); ^{13}C($CDCl_3$, room temp., rel. to $CDCl_3$) δ (**3c**) 151.6 (benzylidene μ-*C*–H).

[§] *Crystal data:* $C_{17}H_6O_{10}W_2$, monoclinic, space group *C2/c*, a = 1729.2(4), b = 702.6(7), c = 3116.2(5) pm, β = 99.13(2)°, $U = 3785 \times 10^{-6}$ pm^3, Z = 8; D_c = 2.59 g cm^{-3}, μ(Mo-K_α) = 129 cm^{-1}, empirical absorption correction; graphite-monochromated Mo-K_α radiation, λ = 71.069 pm. 5950 Independent reflections ($2 \leqslant 2\theta \leqslant 48°$) were measured. The structure was solved by direct methods (SHELX, Syntex XTL) and refined by full-matrix least-squares. Final R 0.031, R_w 0.032 for 2548 reflections with $F_o > 3.926$ (F_o).

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

complexes is novel; the addition of a *nucleophilic* ligand–metal fragment has, however, been demonstrated previously.[5]

We thank the Deutsche Forschungsgemeinschaft for financial support of this work, Dr. H. G. Alt (Universität Bayreuth) and Dr. R. Märkl for the ^{13}C n.m.r. measurements, and J. Riede for the intensity measurements in the *X*-ray analysis.

Received, 10th February 1984; Com. 183

References

1 C. P. Casey and S. W. Polichnowski, *J. Am. Chem. Soc.*, 1977, **99**, 6097; C. P. Casey, S. W. Polichnowski, A. J. Shusterman, and C. R. Jones, *ibid.*, 1979, **101**, 7282.

2 C. P. Casey, S. W. Polichnowski, H. E. Tuinstra, L. D. Albin, and J. C. Calabrese, *Inorg. Chem.*, 1978, **17**, 3045.

3 E. O. Fischer, W. Held, F. R. Kreissl, A. Frank, and G. Huttner, *Chem. Ber.*, 1977, **110**, 656.

4 H. Berke, P. Härter, G. Huttner, and L. Zsolnai, *Chem. Ber.*, 1982, **115**, 695.

5 T. V. Ashworth, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1593; M. Berry, J. A. K. Howard, and F. G. A. Stone, *ibid.*, p. 1601; T. V. Ashworth, M. Berry, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *ibid.*, p. 1615; M. Berry, J. Martin-Gil, J. A. K. Howard, and F. G. A. Stone, *ibid.*, p. 1625; J. A. K. Howard, K. A. Mead, J. R. Moss, R. Navarro, F. G. A. Stone, and P. Woodward, *ibid.*, 1981, 743.