

*tert*-butylmethylamine. These results are the first indication that single electron transfer plays a role in the chemistry of aryl nitrenes.<sup>15</sup>

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### Oxidative Transformation of Monobromotetracarbonyl(alkylidyne) Complexes of Molybdenum and Tungsten into Tribromo(alkylidyne) Complexes

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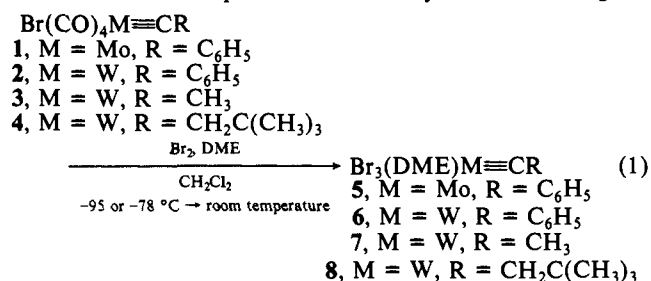
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The chemistry of alkylidyne, or carbyne, complexes of molybdenum and tungsten in high oxidation states has been developed during the past years by Schrock and co-workers. This work has led to the discovery of remarkable reactions such as acetylene metathesis by trisalkoxymetalalkylidyne complexes of tungsten<sup>1</sup> and molybdenum<sup>2</sup> or the formation of cyclopentadienyl ligands in the reaction of trihalotungsten alkylidyne complexes with acetylenes.<sup>3</sup> Most of this chemistry was investigated by using neopentylidyne systems. This restriction originates in the synthetic method used for the preparation of the alkylidyne complexes,  $\alpha$ -hydrogen elimination,<sup>4</sup> which proceeds well only with bulky substituents, e.g., in the preparation of  $(\text{Me}_3\text{CCH}_2)_3\text{M}\equiv\text{CCMe}_3$  ( $\text{M} = \text{Mo}, \text{W}$ ).<sup>2,5</sup> The central compounds for this chemistry, however, are the trichloro complexes, e.g., dimethoxyethane (DME)-stabilized  $\text{Cl}_3(\text{DME})\text{M}\equiv\text{CCMe}_3$  ( $\text{M} = \text{Mo}, \text{W}$ ), which are obtained from the trisneopentyl(neopentylidyne)metal complexes by treatment with  $\text{HCl}$ .<sup>2,5</sup> Essentially all other neopentylidyne complexes can be prepared from these compounds. Analogous complexes containing other alkylidyne ligands apparently are not generally accessible, except the trisalkoxy derivatives which can be prepared by acetylene metathesis.<sup>1,2,6</sup>

On the other hand, the chemistry of the related metal carbyne complexes  $\text{X}(\text{CO})_4\text{M}\equiv\text{CR}$  ( $\text{X} = \text{halide}, \text{M} = \text{Cr}, \text{Mo}, \text{W}; \text{R} = \text{alkyl}, \text{aryl}$ ), developed by Fischer and his group,<sup>7</sup> is much less restricted in the choice of the carbyne, or alkylidyne, ligands. However, no methods are known for the oxidative conversion of monohalotetracarbonylmetal carbyne complexes into trihalometal carbyne complexes.<sup>8</sup> Availability of such procedures would considerably facilitate exploration of the chemistry of metal-carbon triple bonds. We wish to report a simple procedure for

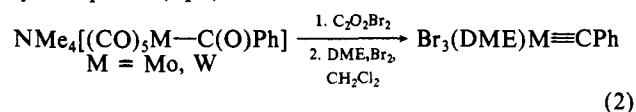
bromine oxidation of  $\text{trans-Br}(\text{CO})_4\text{M}\equiv\text{CR}$  ( $\text{M} = \text{Mo}, \text{W}; \text{R} = \text{alkyl}, \text{aryl}$ ). It provides an efficient general synthesis of tri-bromometal alkylidyne complexes of molybdenum and tungsten in combination with previously developed routes to metal carbyne complexes based on oxide abstraction from acyl ligands<sup>9</sup> and double  $\beta$ -addition of electrophiles to acetylide ligands.<sup>10</sup>

The key step of the successful oxidation is the low-temperature reaction of the *trans*-bromotetracarbonylmetal carbyne complexes,  $\text{Br}(\text{CO})_4\text{M}\equiv\text{CR}$ , **1-4**, with an equivalent amount of bromine in dichloromethane solution. The initial low-temperature intermediates decompose upon warming under loss of carbon monoxide and in the presence of dimethoxyethane the DME stabilized tribromometal alkylidyne complexes  $\text{Br}_3(\text{DME})\text{M}\equiv\text{CR}$ , **5-8**, form. The reactions proceed well for molybdenum and tungsten



systems but not for the chromium analogues.<sup>8</sup> Aliphatic as well as aromatic carbyne ligands are suitable.

The carbyne complexes **1, 2**, and **3** are generated by reaction of the corresponding pentacarbonylmetal acyl complexes  $\text{NMe}_4[(\text{CO})_5\text{M}-\text{C}(\text{O})\text{R}]$  **9, 10**, and **11** (**9**,  $\text{M} = \text{Mo}, \text{R} = \text{C}_6\text{H}_5$ ; **10**,  $\text{M} = \text{W}, \text{R} = \text{C}_6\text{H}_5$ ; **11**,  $\text{M} = \text{W}, \text{R} = \text{CH}_3$ ) with oxalyl bromide in methylene chloride at low temperatures (**9**,  $-78^\circ\text{C}$ ; **10**,  $-78$  to  $-20^\circ\text{C}$ ; **11**,  $-95$  to  $-20^\circ\text{C}$ ).<sup>9</sup> Formed  $\text{NMe}_4\text{Br}$  is removed by filtration at  $-78^\circ\text{C}$ . The initial solutions of the phenylcarbyne complexes **1** and **2** are of sufficient high purity for the direct further reaction with bromine. In succession, a tenfold excess of DME and a cold  $\text{CH}_2\text{Cl}_2$  solution ( $-78^\circ\text{C}$ ) of an equivalent amount of bromine are added. The red reaction solutions of **1** and **2** are allowed to warm up slowly to room temperature. Recrystallization<sup>18</sup> of the products from  $\text{CH}_2\text{Cl}_2$ /pentane affords **5**<sup>11</sup> as brown microcrystals and **6**<sup>12</sup> as dark green crystals in 80% and 90% yield, respectively. Thus, the tribromometal benzylidyne complexes of molybdenum and tungsten are prepared in a single procedure from the easily available pentacarbonylmetal acyl complexes (eq 2).



Analogous direct oxidation of the methylcarbyne complex **3** has not proved to be successful reproducibly. Apparently, already small amounts of impurity in the initial carbyne complex solution—presumably due to decomposition of rather labile **3** or minor side products in the reaction of **11** with oxalyl bromide—adversely affect the reaction with bromine. Thus, compound **3** is purified by chromatographic methods.<sup>13</sup> Similarly, the carbyne complex  $\text{Br}(\text{CO})_4\text{W}\equiv\text{CCH}_2\text{CMe}_3$  (**4**)—obtained by double protonation of  $\text{NEt}_4[(\text{CO})_5\text{W}-\text{C}\equiv\text{CCMe}_3]$  with  $\text{CF}_3\text{SO}_3\text{H}$  and addition of  $\text{NEt}_4\text{Br}$ <sup>10</sup>—is first isolated in pure form.<sup>14</sup> Bromine

(1) (a) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932-3934. (b) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554-1562. (c) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563-1573.

(2) (a) McCullough, L. G.; Schrock, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 4067-4068. (b) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5987-5998.

(3) (a) Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wassermann, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808-6809. (b) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574-1583.

(4) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98-104.

(5) (a) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774-6776. (b) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645-1651.

(6) (a) Schrock, R. R.; Listemann, M. L.; Sturgeooff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291-4293. (b) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74-83. (c) Strutz, H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1600-1601.

(7) Fischer, E. O.; Schubert, U. *J. Organomet. Chem.* **1975**, *100*, 59-81.

(8) Oxidation reactions of  $\text{Br}(\text{CO})_4\text{CrCPh}$  with strong oxidizing agents such as  $\text{Cl}_2$  or  $\text{Br}_2$  have been reported. Only complete degradation of the complex was observed. Fischer, E. O.; Ruhs, A.; Kalder, H. J. *Z. Naturforsch., B* **1977**, *32B*, 473-475.

(9) Mayr, A.; McDermott, G. A.; Dorries, A. M. *Organometallics* **1985**, *3*, 608-610.

(10) Mayr, A.; Schaefer, K. C.; Huang, E. Y. *J. Am. Chem. Soc.* **1984**, *106*, 1517-1518.

(11) **5**: Anal. Calcd for  $\text{C}_{11}\text{H}_9\text{Br}_3\text{O}_2\text{Mo}$ : C, 25.66; H, 2.94; Br, 46.56. Found: C, 25.50; H, 3.03; Br, 46.87. <sup>13</sup>C NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-20^\circ\text{C}$ )  $\delta$  329.2 (CPh).

(12) **6**: Anal. Calcd for  $\text{C}_{11}\text{H}_9\text{Br}_3\text{O}_2\text{W}$ : C, 21.92; H, 2.51; Br, 39.77. Found: C, 21.72; H, 2.51; Br, 39.75. <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.62, 6.89, 6.69 (m, 5,  $\text{C}_6\text{H}_5$ ), 4.28, (s, 3,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ ), 4.13 (m, 2,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ ), 4.04 (m, 2,  $\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_3$ ), 3.99 (s, 3,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ ), <sup>13</sup>C NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  331.7 ( $J_{\text{CW}} = 219$  Hz), 138.6, 132.6, 126.5 ( $\text{C}_6\text{H}_5$ ), 79.6, 76.2, 70.7, 61.2 ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ ).

(13) Fischer, E. O.; Kreis, G. *Chem. Ber.* **1976**, *109*, 1673-1683.

oxidation of the alkyl-substituted carbene complexes **3** and **4** is achieved at  $-95\text{ }^{\circ}\text{C}$ . The initially dark red solutions turn orange brown upon warming to room temperature. The products are recrystallized<sup>18</sup> from  $\text{CH}_2\text{Cl}_2$ /pentane and obtained as dark green **7**<sup>15</sup> and dark turquoise **8**<sup>16</sup> microcrystals in 70% and 50% yield, respectively. The new alkylidyne complexes **5-8** are thermally stable but very sensitive toward the atmosphere.

With the oxidation reaction described in this paper and the methods developed earlier<sup>9,10</sup> thermally stable carbene complexes of both known types of the group 6<sup>17</sup> transition metals are now easily accessible. The *trans*-halotetracarbonylmetal carbene complexes, while rather thermally labile themselves,<sup>7</sup> prove to be the critical intermediates in these synthetic procedures.

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(14) **4**: Chromatography on silica at  $-40\text{ }^{\circ}\text{C}$ , eluted with pentane/ $\text{CH}_2\text{Cl}_2$ , 5:2. <sup>13</sup>C NMR ( $\text{CDCl}_3$ ,  $-40\text{ }^{\circ}\text{C}$ )  $\delta$  293.9 ( $J_{\text{CW}} = 172.3\text{ Hz}$ ,  $\text{CCH}_2\text{CMe}_3$ ), 192.1 ( $J_{\text{CW}} = 129.1\text{ Hz}$ , CO).

(15) **7**: Anal. Calcd for  $\text{C}_6\text{H}_{13}\text{Br}_3\text{O}_2\text{W}$ : C, 13.33; H, 2.42; Br, 44.33. Found: C, 13.34; H, 2.33; Br, 45.99. <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.32 (s, 3,  $^3J_{\text{WH}} = 9.8\text{ Hz}$ ,  $\text{CCH}_3$ ); <sup>13</sup>C NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-20\text{ }^{\circ}\text{C}$ )  $\delta$  337.5 ( $J_{\text{CW}} = 219\text{ Hz}$ , CMe).

(16) **8**: Anal. Calcd for  $\text{C}_{10}\text{H}_2\text{Br}_3\text{O}_2\text{W}$ : C, 20.12; H, 3.55. Found: C, 20.14; H, 3.77. <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.41 (s, 2,  $^3J_{\text{WH}} = 7\text{ Hz}$ ,  $\text{CCH}_2\text{CMe}_3$ ); <sup>13</sup>C NMR ( $\text{CDCl}_3$ ,  $-20\text{ }^{\circ}\text{C}$ )  $\delta$  345.4 ( $J_{\text{CW}} = 215\text{ Hz}$ ,  $\text{CCH}_2\text{CMe}_3$ ).

(17) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III  $\rightarrow$  3 and 13.)

(18) After removal of the solvent from the reaction solution the dark orange-brown solid is taken up in a small amount of  $\text{CH}_2\text{Cl}_2$  (typically 5 mL of  $\text{CH}_2\text{Cl}_2$  per mmol of product) and precipitated with pentane (3 $\times$  to 4 $\times$  the volume of  $\text{CH}_2\text{Cl}_2$  present). This precipitation procedure is repeated two or three times. The resulting solid (orange-brown, **5**; deep green, **6-8**) is taken up in a small amount of  $\text{CH}_2\text{Cl}_2$ , cooled to  $0\text{ }^{\circ}\text{C}$ , and filtered to remove any insolubles. Pentane is added to the resulting solution to precipitate the product as a microcrystalline powder. For R = alkyl the initial precipitate is removed as well by filtration when it is oily.

## Zirconoxycarbene Complexes of Ruthenium—Reduction of Coordinated CO in the Reaction of a Zr–Ru Compound with $\text{H}_2$

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We have synthesized compounds with directly bonded early and late transition metals such as  $\text{Cp}_2\text{Zr}[\text{Ru}(\text{CO})_2\text{Cp}]_2$  (**1**) in the hope of cleaving the metal–metal bond with  $\text{H}_2$ .<sup>1</sup> The resulting mixture containing reactive hydridic M–H and acidic M–H units might be a powerful reducing system for polar molecules including CO. Here we present evidence for a circuitous stepwise conversion of **1** into Ru–H and Zr–H units and for the reduction of coordinated CO to a formyl or zirconoxy carbene group.

Previously, we reported that **1** reacts with ethylene or with CO to form the strained, reactive adducts **2** or **3** and to expel

(1) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *Organometallics* **1984**, *3*, 504.

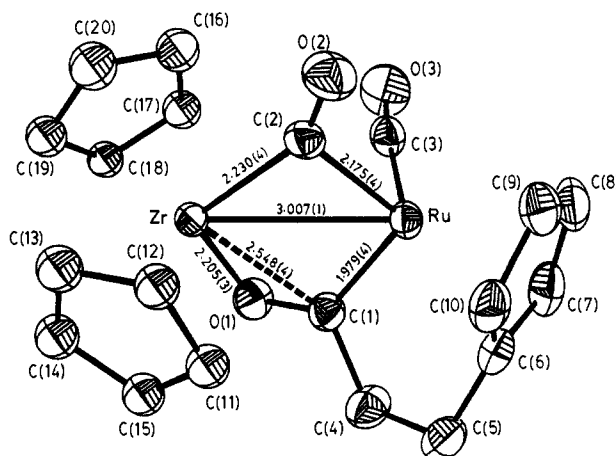
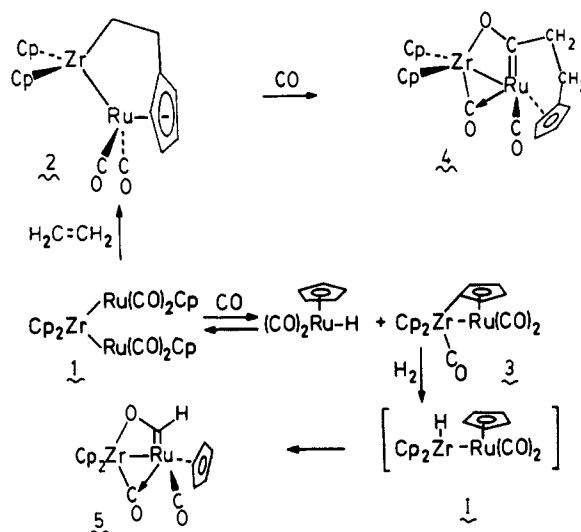


Figure 1. Molecular structure and labeling scheme for **4**.

$\text{CpRu}(\text{CO})_2\text{H}$ .<sup>2</sup> Here we report that the reaction of **2** with CO and the reaction of **3** with  $\text{H}_2$  produce zirconoxycarbene complexes of ruthenium.



When an amber  $\text{C}_6\text{D}_6$  solution of ethylene product **2** was treated with CO (700 mm), the solution slowly turned dark red. <sup>1</sup>H NMR demonstrated that **2** was converted to **4** without the intervention of a detectable intermediate ( $t_{1/2} \approx 15\text{ h}$ ). Crystalline **4** was isolated in 80% yield from the reaction of **2** with CO (760 mm) in toluene at  $55\text{ }^{\circ}\text{C}$  for 30 h. The structure of **4** was determined by single-crystal X-ray diffraction (Figure 1).<sup>3</sup>

The metals in **4** are linked by a direct Zr–Ru bond (3.007 Å), by a zirconoxycarbene bound to Ru (which can also be regarded as a Zr-complexed Ru–acyl), and by a semibridging carbonyl bound strongly to Zr. The metrical details of this semibridging carbonyl are similar to those in  $\text{Cp}_2\text{Zr}(\text{CO})(\mu\text{-}\eta^1(\text{Zr}),\eta^5\text{-C}_5\text{H}_4)\text{-Ru}(\text{PMe}_3)(\text{CO})$ .<sup>2</sup>

The key spectral features of **4** which characterize its structural type are the <sup>13</sup>C NMR and IR parameters associated with the carbonyl ligands and the zirconoxycarbene ligand.<sup>4</sup> In the <sup>13</sup>C NMR of **4**, the terminal ruthenium CO appears at  $\delta$  205, the semibridging CO appears at  $\delta$  316, and the carbene carbon appears at  $\delta$  279 as a peak significantly broadened by unresolved two-bond

(2) Casey, C. P.; Palermo, R. E.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 4597.

(3) See the supplementary material for details of X-ray crystallography.

(4) <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>)  $\delta$  5.71 (s, 5 H, CpZr), 5.62 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 5.06 (s, 5 H, CpZr), 4.94 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.81 (m, 1 H, C<sub>5</sub>H<sub>4</sub>) 4.35 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 3.62 (dt,  $J = 18, 8\text{ Hz}$ , 1 H, C(O)CHH), 2.92 (ddd,  $J = 18, 8, 4\text{ Hz}$ , 1 H, C(O)CHH), 1.75 (ddd,  $J = 14, 10, 4\text{ Hz}$ , 1 H, C(O)CH<sub>2</sub>CHH), 1.42 (dt,  $J = 12, 9\text{ Hz}$ , 1 H, C(O)CH<sub>2</sub>CHH). <sup>13</sup>C{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>,  $26\text{ }^{\circ}\text{C}$ )  $\delta$  316 ( $\mu\text{-CO}$ ), 279 (ZrOC=RU), 205 (RuCO), 127 (C, of C<sub>5</sub>H<sub>4</sub>), 108 (CpZr), 105 (CpZr), 104 (CH<sub>2</sub>), 92, 89, 84, 79 (C<sub>5</sub>H<sub>4</sub>), 22 (CH<sub>2</sub>).