

### Chemical and Electrochemical Reduction of CycloheptatrieneW(CO)<sub>3</sub>\*

N. EL MURR\*\*, M. RIVECCIÉ

*Laboratoire de Polarographie Organique associé au CNRS (LA 33), Faculté des Sciences Gabriel, 6, boulevard Gabriel, 21100 Dijon, France*

A. SALZER

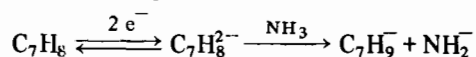
*Anorganisch chemisches Institut der Universität Zürich, CH 8001 Zürich, Switzerland*

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Our previous work on C<sub>7</sub>H<sub>8</sub>W(CO)<sub>3</sub> [1] and C<sub>7</sub>H<sub>8</sub>Mo(CO)<sub>3</sub> [2] showed that cationic cycloheptadienyl compounds were easily obtained by protonation reactions and that the tungsten complexes were far more stable than the corresponding molybdenum complexes.

In view of a recent article by Hoffman [3] on the potential structure and stability of (C<sub>6</sub>H<sub>7</sub>Cr(CO)<sub>3</sub>)<sup>-</sup> and the series of papers by Semmelhack [4] in which he describes the nucleophilic addition of carbanions to C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub> giving compounds of the general type (C<sub>6</sub>H<sub>6</sub>RCr(CO)<sub>3</sub>)<sup>-</sup> as unstable intermediates, we attempted a chemical and electrochemical preparation of (C<sub>7</sub>H<sub>9</sub>W(CO)<sub>3</sub>)<sup>-</sup> with the assumption that this anion might be more stable than the above intermediates.

Hafner and Rellensmann [5] have shown that cycloheptatriene is readily reduced by alkali metals in liquid ammonia to the stable C<sub>7</sub>H<sub>9</sub><sup>-</sup>, the proposed mechanism being:



We therefore treated C<sub>7</sub>H<sub>8</sub>W(CO)<sub>3</sub> under the same conditions with two equivalents of Na in liquid ammonia, expecting a similar reaction to occur with coordinated cycloheptatriene, although no such reaction was known in metallorganic chemistry.

After addition of THF to this mixture and evaporation of the ammonia a yellow-brown solution was obtained.

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\*\*Address all correspondence to: Dr. N. El Murr, Université de Dijon, Faculté des Sciences Gabriel, Laboratoire de Polarographie Organique, 6, boulevard Gabriel, 21100 Dijon (France).

As a proof of the existence of (C<sub>7</sub>H<sub>9</sub>W(CO)<sub>3</sub>)<sup>-</sup> we treated this solution with methyl iodide in order to obtain C<sub>7</sub>H<sub>9</sub>W(CO)<sub>3</sub>CH<sub>3</sub> in analogy to reaction of (C<sub>5</sub>H<sub>5</sub>W(CO)<sub>3</sub>)<sup>-</sup> giving C<sub>5</sub>H<sub>5</sub>W(CO)<sub>3</sub>CH<sub>3</sub> [6].

We were indeed able to isolate C<sub>7</sub>H<sub>9</sub>W(CO)<sub>3</sub>CH<sub>3</sub> as a yellow solid by extraction with hexane and crystallisation at low temperatures. Its IR and NMR spectra as well as the elemental analysis are consistent with the proposed structure and resemble closely the corresponding cyclopentadienyl compound.

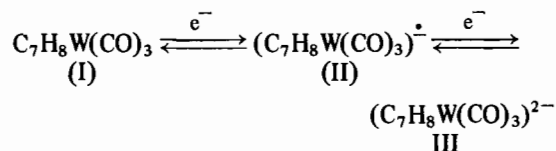
In view of the poor yield of this reaction we undertook also an electrochemical study of C<sub>7</sub>H<sub>8</sub>W(CO)<sub>3</sub>. The use of electrochemistry for preparative metallorganic reactions has not yet received much attention [7 - 8]. In a recent report [9] we described the quantitative reduction of C<sub>8</sub>H<sub>8</sub>Fe(CO)<sub>3</sub> to C<sub>8</sub>H<sub>10</sub>Fe(CO)<sub>3</sub> by electrochemical means, which indicated the superiority of this method over conventional preparative techniques.

The polarogram of C<sub>7</sub>H<sub>8</sub>W(CO)<sub>3</sub> in THF with tetrabutylammoniumhexafluorophosphate as supporting electrolyte exhibits two distinct reduction waves (E<sub>1/2</sub> = -1.52 and -2.55 V SCE) and one oxidation wave (E<sub>1/2</sub> = +0.74 V SCE).

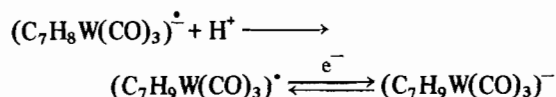
The heights of these two cathodic waves are not equivalent; on comparison with the reported waves for C<sub>8</sub>H<sub>8</sub>Fe(CO)<sub>3</sub> [9] for the same concentration it is apparent that the wave at -1.52 V corresponds to more than one electron and the other wave at -2.55 V to less, the sum of both being however equivalent to two electrons. The addition of proton donors like H<sub>2</sub>O, phenol or benzoic acid causes the displacement of the second wave to a more positive potential and the polarogram shows then only one two-electron wave.

By using cyclic voltammetry on mercury electrode in the absence of a proton donor the two stages of the reduction are reversible if the scanning rate is 10 V/sec.

We therefore suggest the following mechanism for the electrochemical reduction under aprotic conditions:



In the presence of a proton donor the protonation of the radical anion II occurs before the second reduction step. In this case (C<sub>7</sub>H<sub>9</sub>W(CO)<sub>3</sub>)<sup>•</sup> is formed and immediately reduced to the corresponding anion.



The presence of a proton either from the solvent, the electrolyte or a trace amount of water can explain the different height of the two reduction waves under "aprotic" conditions, as the above reaction can then occur at least partially. To confirm this mechanism we repeated the electrochemical reduction at  $-1.5$  V on a preparative scale in the presence of a proton donor.

A yellow solution was obtained and addition of methyl iodide to this solution led to the formation of  $C_7H_9W(CO)_3CH_3$  in 80% yield, identical with the compound described above.

These results indicate that the anionic cycloheptadienyl tungsten tricarbonyl is more stable than the corresponding cyclohexadienyl complexes postulated by Semmelhack [4] as it can be generated *in situ* in room temperature solutions. It represents the first example of a Birch-type reduction of a coordinated olefin in liquid ammonia and completes the iso-electronic series  $(C_7H_9Fe(CO)_3)^+$ ,  $C_7H_9Mn(CO)_3$ ,  $(C_7H_9W(CO)_3)^-$ .

We are continuing our research into the reactivity of this interesting new compound.

### Experimental

All experiments were carried out under dry nitrogen or argon.

$(C_4H_9)NPF_6$  was heated to the melting point and dried under vacuum. THF for the electrochemical experiments was dried over Na/benzophenone and distilled directly into the electrochemical cell prior to use.

The IR was recorded on a Beckman IR 12, the NMR on a JEOL 60 HL instrument.

$C_7H_9W(CO)_3CH_3$

IR:  $\nu(CO)$ : 1936, 1949, 2025  $cm^{-1}$  in hexane.

NMR: ( $C_6D_6$ ,  $\delta$  ppm): 4.9 (1 H, tt), 4.3 (2H, dd), 3.8 (2H, m), 1.6 (4H, m), 0.9 (3H, s).

Anal.: Found: C, 34.95; H, 3.24; W, 48.84.  $C_{11}H_{12}O_3W$ . Calc.: C, 35.13; H, 3.21; W, 48.88%.

### Acknowledgements

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