

## New Routes To Molybdenum and Tungsten Carbyne Complexes [M(CO)<sub>2</sub>(=CPh)(η-C<sub>5</sub>H<sub>4</sub>R)] (M = Mo or W, R = SnPh<sub>3</sub>; M = W, R = H)

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Treatment of the ethoxy carbenes [M(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Ph}(η-C<sub>5</sub>H<sub>5</sub>)] (M = Mo or W) with LDA or LDA/HMPA followed by PhC(=O)Cl results in the carbyne complexes [M(CO)<sub>2</sub>(=CPh)(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)] via the anions [M(CO)<sub>2</sub>{=C(OEt)Ph}(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)]<sup>-</sup>, while treatment of [W(SnPh<sub>3</sub>)(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)] with LiPh followed by TMEDA/MeC(=O)Cl results in the carbyne [W(CO)<sub>2</sub>(=CPh)(η-C<sub>5</sub>H<sub>5</sub>)].

Carbyne complexes of the type [M(CO)<sub>2</sub>(=CR)(η-C<sub>5</sub>H<sub>5</sub>)] (M = Mo, W; R = alkyl, aryl) are of great interest, as are convenient syntheses of them. We present here two new routes to these complexes that are based upon two new exploitations of carbene chemistry.

The first of these routes is based upon anionic carbene complexes of the type [ML<sub>n</sub>(=CR<sup>1</sup>R<sup>2</sup>)]<sup>-</sup>. These are promising reagents that we have utilized to make a number of complexes of the type [MR(CO)<sub>2</sub>(=CR<sup>1</sup>R<sup>2</sup>)(η-C<sub>5</sub>H<sub>5</sub>)] in which R (R = H, Me, CH<sub>2</sub>Ph, etc.) subsequently undergoes migration to the carbene.<sup>1-6</sup> To date, formation of the anions [M(CO)<sub>2</sub>(=CR<sup>1</sup>R<sup>2</sup>)(η-C<sub>5</sub>H<sub>5</sub>)]<sup>-</sup> relied upon the reduction of the corresponding iodide [MI(CO)<sub>2</sub>(=CR<sup>1</sup>R<sup>2</sup>)(η-C<sub>5</sub>H<sub>5</sub>)] with NaC<sub>10</sub>H<sub>8</sub>.<sup>7</sup> Unfortunately such iodide complexes are not always readily available. We give here a new route to anionic carbene complexes that does not involve iodo carbene complexes and show further, that reactions of the resulting anions result in hydride-to-carbene migration processes as well as formation of carbyne derivatives.

Reactions of [M(SnPh<sub>3</sub>)(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)] (M = Mo **1** or W **2**) or [Fe(SnPh<sub>3</sub>)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)] with LiBu<sup>n</sup> or LDA proceed by deprotonation of the cyclopentadienyl ring to form M(η-C<sub>5</sub>H<sub>4</sub>Li) intermediates<sup>8-10</sup> from which migration of the SnPh<sub>3</sub> group to the ring results in formation of the anions [M(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)]<sup>-</sup> (M = Mo or W) or [Fe(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)]<sup>-</sup>. Reagents such as LiBu<sup>n</sup> are not appropriate for carbene complexes such as [M(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Ph}(η-C<sub>5</sub>H<sub>5</sub>)] (M = Mo **3** or W **4**) since the result is attack of the organolithium reagent at the carbene atom. This is clearly shown in the reaction of LiMe with [W(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Ph}(η-C<sub>5</sub>H<sub>5</sub>)] followed by acid which affords the alkylidene [W(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(Me)Ph}(η-C<sub>5</sub>H<sub>5</sub>)].<sup>2</sup> However, addition of LDA to a solution of **3** results in two new bands

in the IR spectrum of the reaction mixture [ $\nu_{\text{CO}}/\text{cm}^{-1}$  (THF) 1846 and 1678] at positions very similar to those of the anion [Mo(CO)<sub>2</sub>{=C(OEt)Ph}(η-C<sub>5</sub>H<sub>5</sub>)]<sup>-</sup> formed in the reaction of [MoI(CO)<sub>2</sub>{=C(OEt)Ph}(η-C<sub>5</sub>H<sub>5</sub>)] with Na(C<sub>10</sub>H<sub>8</sub>). These bands are therefore assigned to the anion [Mo(CO)<sub>2</sub>{=C(OEt)Ph}(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)]<sup>-</sup> **5**. There are also two minor, non-anion signals in the IR spectrum [ $\nu_{\text{CO}}/\text{cm}^{-1}$  (THF) 1993 and 1923]. Addition of MeCO<sub>2</sub>H to the reaction mixture results in disappearance of the anion bands and formation of the crystallographically characterized (Fig. 1) [Mo(CO)<sub>2</sub>(η<sup>3</sup>-PhCHOEt)(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)]<sup>+</sup> **6**<sup>+</sup> over 2 h. The crystal structure shows that the disposition of the benzyl is similar to that of the corresponding tungsten complex [W(CO)<sub>2</sub>(η<sup>3</sup>-PhCHOEt)(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)]<sup>+</sup> **5**. The two bands at 1993 and 1923 cm<sup>-1</sup> also disappear on the addition of acid. By analogy to protonation reactions of [Mo(CO)<sub>2</sub>{=C(OEt)Ph}(η-C<sub>5</sub>H<sub>5</sub>)]<sup>-</sup> reported earlier,<sup>5</sup> protonation of [Mo(CO)<sub>2</sub>{=C(OEt)Ph}(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)]<sup>-</sup> affords a metal hydride **7** (not detected) as the first product. This rearranges by the mechanism shown in Scheme 1 to give the η<sup>3</sup>-benzyl **6**. In support of this, two bands in the IR spectrum [ $\nu_{\text{CO}}/\text{cm}^{-1}$  (THF) 1929 and 1835] assigned to complex **8** are formed rapidly after protonation. These decline in intensity over 2 h to leave the only isolable product, **6**.

The corresponding reaction of the tungsten complex **4** gives only a low yield (5–10%) of the analogous η<sup>3</sup>-benzyl complex **9** together with some recovered starting material. In this case the higher frequency bands in the IR spectrum of the anion solution represent an isolable product (9% recrystallized yield) characterized as the new carbyne complex [W(CO)<sub>2</sub>(=CPh)(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)] **10**. A shorter exposure of the starting material **4** to LDA prior to addition of MeCO<sub>2</sub>H enhances the yield of **9** relative to the carbyne **10**, but with more recovered starting material. A longer exposure of **4** to LDA prior to addition of

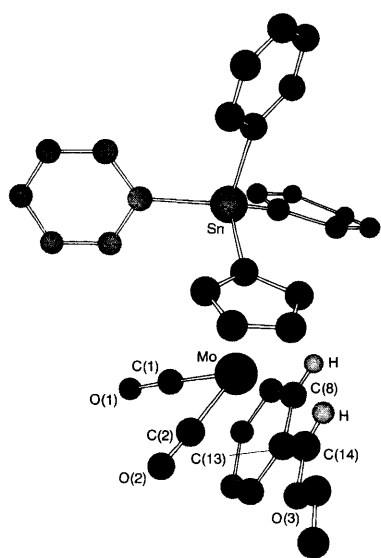
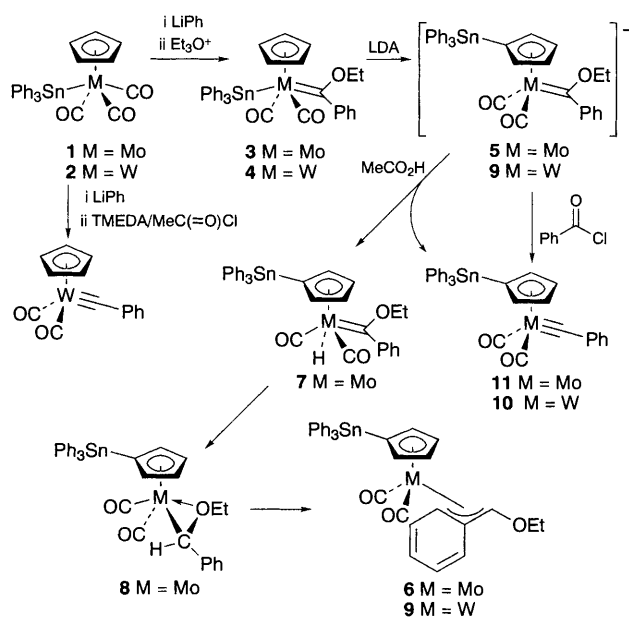


Fig. 1 Molecular structure of [Mo(CO)<sub>2</sub>(η<sup>3</sup>-PhCHOEt)(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)] **6**. Selected bond lengths (Å): Mo–C(1) 1.929(16), Mo–C(2) 1.873(17), Mo–C(8) 2.420(16), Mo–C(13) 2.377(19), Mo–C(14) 2.310(15).



Scheme 1

MeCO<sub>2</sub>H gives a higher yield of the carbyne **10**, less of the benzyl **9**, and less recovered starting material. Complex **10** is a substituted cyclopentadienyl analogue of the well known complexes [W(CO)<sub>2</sub>(≡CR)(η-C<sub>5</sub>H<sub>5</sub>)] (R = Ph, MeC<sub>6</sub>H<sub>4</sub>).<sup>11</sup>

This reaction may be diverted entirely towards carbyne **10** through the use of benzoyl chloride instead of MeCO<sub>2</sub>H. In this case, the isolated yield of the carbyne **10** is 37%. In analogous fashion, the yield of the molybdenum carbyne **11**‡ is 35%. Complex **11** is reasonably stable and can be stored for a few days at ambient temperature under nitrogen. The X-ray crystal structure of complex **11** is shown in Fig. 2 and represents a comparatively rare example of a crystallographically characterized carbyne [Mo(CO)<sub>2</sub>(≡CR)(η-C<sub>5</sub>H<sub>4</sub>R)]. The X-ray crystal structure of complex **10** (not illustrated)§ shows that the two complexes **10** and **11** are essentially isostructural and that the M≡C bonds are similar in length. A comparison of the IR spectrum of **11** with the reaction mixture containing the molybdenum anion **5** (above) suggests that the two high frequency signals present in its spectrum are due to complex **11**.

The second carbyne synthesis presented here is a convenient, high yield, new synthesis of the unsubstituted carbyne complex [W(CO)<sub>2</sub>(≡CPh)(η-C<sub>5</sub>H<sub>5</sub>)]<sup>11</sup> that also proceeds via a carbene methodology. Treatment of [W(SnPh<sub>3</sub>)(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)] with LiPh gives the known acyl [W(SnPh<sub>3</sub>)(COPh)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)]<sup>-</sup>.<sup>12-14</sup> Addition of TMEDA/MeC(=O)Cl to this anion at -78 °C results in three new bands in the IR spectrum of the reaction mixture [ν<sub>CO</sub>/cm<sup>-1</sup> (CH<sub>2</sub>Cl<sub>2</sub>) 1949, 1885 and 1746]. Warming to ambient temperature, followed by stirring for several hours, results in the formation of [W(CO)<sub>2</sub>(≡CPh)(η-C<sub>5</sub>H<sub>5</sub>)] in a 78% recrystallised but unoptimized yield. It is likely that acetylation of the acyl [W(SnPh<sub>3</sub>)(COPh)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)]<sup>-</sup> results in a reactive carbene [W(SnPh<sub>3</sub>){=C(OCOMe)Ph}(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)] (responsible for the IR spectrum after acetylation) which collapses through loss of the SnPh<sub>3</sub> (probably as SnClPh<sub>3</sub>) and O<sub>2</sub>CMe (probably as LiO<sub>2</sub>CMe) fragments to form the final product. The loss of acetate in this fashion is somewhat reminiscent of the formation of octahedral carbyne complexes [M(≡CR)X(CO)<sub>2</sub>L<sub>2</sub>] [X = Cl, Br; L<sub>2</sub> = py<sub>2</sub>, tmeda, bpy] from [NMe<sub>4</sub>][M{C(O)R}(CO)<sub>5</sub>] (R = Ph, M = Cr, Mo,

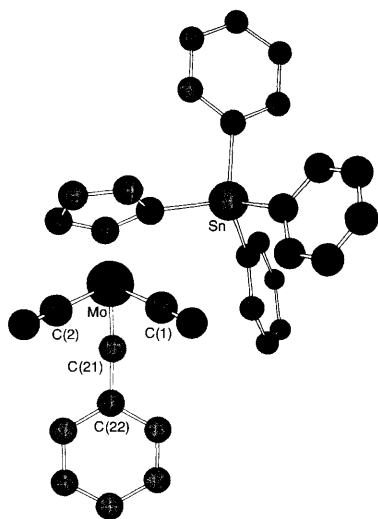


Fig. 2 Molecular structure of [Mo(CO)<sub>2</sub>(≡CPh)(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)] **11**. Selected bond lengths (Å): Mo–C(1) 1.964(21), Mo–C(2) 1.962(18), Mo–C(21) 1.810(14), C(21)–C(22) 1.495(20). For the corresponding complex **10**, selected bond lengths (Å): W–C(1) 1.970(31), W–C(2) 2.064(33), W–C(21) 1.864(28), C(21)–C(22) 1.483(38).

W; R = Me, M = W) but the loss of SnPh<sub>3</sub> is a key step in the method that we present here.<sup>15-17</sup>

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## Footnotes

† [Mo(CO)<sub>2</sub>(η<sup>3</sup>-PhCHOEt)(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)] **6**. *Crystal data*: monoclinic, space group *P*2<sub>1</sub>/*c* (*C*<sub>2h</sub><sup>5</sup>, no. 14), *a* = 9.934(6), *b* = 9.925(6), *c* = 30.724(25) Å, β = 94.97(6)°, *U* = 3017(3) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.32 g cm<sup>-3</sup>, Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 12.67 cm<sup>-1</sup>, *F*(000) = 1400. Data were collected in the range 3.5 < 2θ < 50° (ω-scans), 2815 independent reflections [|*F*|/σ(|*F*|) > 3.0]. Final *R* = 0.0911 (*R*<sub>w</sub> = 0.0718, 352 parameters, mean and maximum δ/σ 0.004, 0.021), with allowance for the thermal anisotropy of all nonhydrogen atoms.

‡ [Mo(CO)<sub>2</sub>(≡CPh)(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)] **11**. *Crystal data*: space group *P*1̄ (*C*<sub>1</sub><sup>1</sup>, no. 2), triclinic, *a* = 9.908(12), *b* = 11.803(9), *c* = 14.268(12) Å, α = 87.92(7)°, β = 74.34(8)°, γ = 65.83(8)°, *U* = 1460.5(7) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.490 g cm<sup>-3</sup>, Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 13.09 cm<sup>-1</sup>, *F*(000) = 648. Data were collected in the range 3.5 < 2θ < 50° (ω-scans), 2608 independent reflections [|*F*|/σ(|*F*|) > 3.0]. Final *R* = 0.0725 (*R*<sub>w</sub> = 0.1019, 325 parameters, mean and maximum δ/σ 0.036, 0.006), with allowance for the thermal anisotropy of all non-hydrogen atoms.

§ *Crystal data*: [W(CO)<sub>2</sub>(≡CPh)(η-C<sub>5</sub>H<sub>4</sub>SnPh<sub>3</sub>)] **10**, C<sub>32</sub>H<sub>24</sub>O<sub>2</sub>SnW triclinic, space group *P*1̄ (*C*<sub>1</sub><sup>1</sup>, no. 2), *a* = 10.073(14), *b* = 11.826(9), *c* = 14.233(8) Å, α = 87.83(5)°, β = 74.10(8)°, γ = 65.54(8)°, *U* = 1479(2) Å<sup>3</sup>, *D*<sub>c</sub> = 1.490 g cm<sup>-3</sup>, *Z* = 2, Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 48.42 cm<sup>-1</sup>, *F*(000) = 712. Data were collected in the range 3.5 < 2θ < 45° (ω-scans), 2116 independent reflections [|*F*|/σ(|*F*|) > 4.0]. *R* = 0.0891, all non-hydrogen atoms anisotropic.

Atomic coordinates, bond lengths and angles, and thermal parameters for **6**, **10** and **11** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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