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Reactions of α-lithio (aminocarbene)tungsten anions with diiodoalkanes: synthesis of (μ-bis(aminocarbene))ditungsten complexes

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Abstract

Treatment of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (**1**) with ^nBuLi followed by 5–10 equiv. of a diiodoalkane (diiodomethane, 1,2-diiodoethane, 1,3-diiodopropane, 1,4-diiodobutane, or 1,5-diiodopentane) gave the respective (iodoalkylaminocarbene)tungsten complexes $(CO)_5W[C(N(CH_3)_2)CH_2(CH_2)_nI]$ ($n = 1$–5) (**2**). For the reaction of the α-lithio anion of **1** with diiodomethane, only a 5% yield of the corresponding complex **2a** ($n = 1$) was obtained. Moreover, the reaction of the α-lithio anion of **1** with 1,2-diiodoethane gave no product **2b** ($n = 2$). On the other hand, good to excellent yields (69–93%) of complexes **2c–e** ($n = 3$–5) were obtained using 1,3-diiodopropane, 1,4-diiodobutane, or 1,5-diiodopentane. Complexes **2c–e** were further treated with the α-lithio anion of **1** to afford the new (μ-bis(aminocarbene))ditungsten complexes $(CO)_5W[C(N(CH_3)_2)CH_2(CH_2)_nCH_2C(N(CH_3)_2)]W(CO)_5$ ($n = 3$–5) (**3c–e**) in yields ranging from 52 to 61%.

Introduction

During the course of our studies to develop methods of synthesizing new (μ-bis(carbene))dimetal complexes [1], we found that α-lithio (alkylaminocarbene)-tungsten complexes readily reacted, in a sequential manner, with diiodoalkanes to produce several new (μ-bis(carbene))ditungsten complexes. Our interest in preparing such systems stems from the fact that dimeric transition metal carbene complexes, in general, are beginning to receive attention because of their use in organic synthesis [1a,2], their mechanisms of formation [3], and as intermediates in the conversion of cyclohexane to benzene on platinum surfaces [4]. Moreover, there are many recent accounts on the use of monomeric (aminocarbene)metal complexes in the application of organic synthesis [5].

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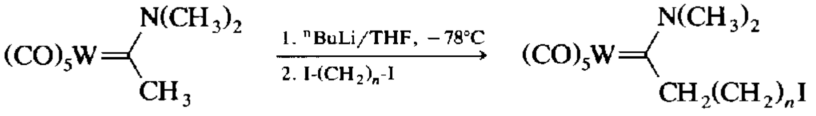
Results and discussion

The reactions of (alkylalkoxycarbene)metal α-anions with electrophilic reagents are well established in the literature [6]. In contrast, there are considerably fewer examples of similar reactions of (alkylaminocarbene)metal α-anions [5h,7]. Moreover, to the best of our knowledge, there are no previous examples of α-lithio (alkylcarbene)metal anions (alkoxy or amino) reacting with difunctional electrophilic reagents to produce (μ-bis(carbene))dimetal complexes [8*]. In the current investigation, the α-lithio (alkylaminocarbene)tungsten anion $(CO)_5W[C(N(CH_3)_2)CH_2]Li$ was generated by treating **1** with ^nBuLi in THF at −78°C [7a]. Subsequently, this α-lithio anion was quenched with 5–10 equiv. of several different diiodoalkanes to afford complexes **2** (eq. 1).



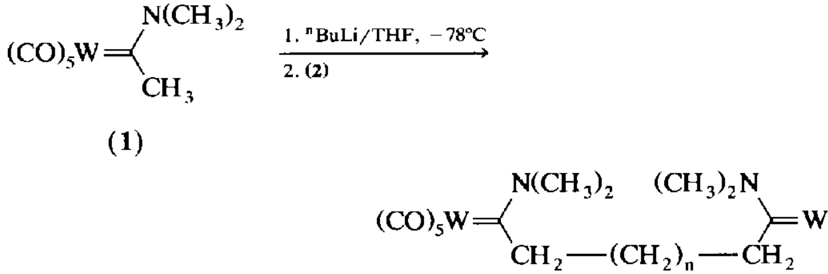
$$(CO)_5W{=}C(N(CH_3)_2)CH_3 \xrightarrow[2.\ I\text{-}(CH_2)_n\text{-}I]{1.\ ^nBuLi/THF,\ -78^\circ C} (CO)_5W{=}C(N(CH_3)_2)CH_2(CH_2)_nI \quad (1)$$

(1) (2)

2	n	% Yield
a	1	5
b	2	–
c	3	93
d	4	69
e	5	79

In general, the yields were much better for 1,3-diiodopropane and higher homologues than for either diiodomethane or 1,2-diiodoethane. In fact, no product was obtained from the reaction of the latter diiodoalkane with the α-lithio anion of **1**. Interestingly, whereas **2a** and **2c** were obtained as yellow crystalline substances, **2d** and **2e** were obtained as yellow oils.

Having complexes **2** in hand allowed for their conversions to (μ-bis(aminocarbene))ditungsten complexes **3** (eq. 2).



$$(CO)_5W{=}C(N(CH_3)_2)CH_3 \xrightarrow[2.\ (2)]{1.\ ^nBuLi/THF,\ -78^\circ C} (CO)_5W{=}C(N(CH_3)_2)CH_2{-}(CH_2)_n{-}CH_2C(N(CH_3)_2){=}W(CO)_5 \quad (2)$$

(1)

(3)

3	n	% Yield
c	3	61
d	4	58
e	5	52

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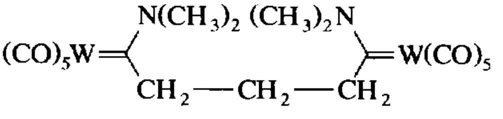
* Reference number with asterisk indicates a note in the list of references.

Thus, treatment of either **2c**, **2d**, or **2e** with the α-lithio anion of **1** produced the respective complexes **3c**, **3d**, and **3e** in good yields. Complexes **3c–e** were all obtained as yellow solids in pure form through flash chromatography. Because of the low yields associated with the preparation of **2a**, its conversion to **3a** (using the α-lithio anion of **1**) was not undertaken. Furthermore, a procedure for the preparation of **3a** (46% yield) has already been developed, which involved the conjugate addition of the α-lithio anion of **1** to the α,β-unsaturated carbene complex $(CO)_5W[C(N(CH_3)_2)CH{=}CH_2]$ [1c].



(3a)

The structures of complexes **2a**, **c–e** and **3c–e** were easily determined through ^1H NMR, ^{13}C NMR, and MS spectroscopic techniques; moreover, the observed spectral values were similar to other (aminocarbene)tungsten complexes [5j,7a,10,11a]. Typically, because of rotational barriers associated with the C(carbene)–N partial double bond [12], two different alkyl resonances are observed in the ^1H and ^{13}C NMR spectra of [(dialkylamino)carbene]tungsten complexes [11]. For example, in **2a** the methyl resonances of the $N(CH_3)_2$ group are observed at δ 3.80 (cis to the $W(CO)_5$ fragment) and 3.35 (trans to the $W(CO)_5$ fragment) in the ^1H NMR spectrum ($CDCl_3$). Furthermore, two ^{13}C NMR signals are seen at approx. δ 52–56 and δ 40–42 for the magnetically nonequivalent methyl carbons in complexes **2a**, **c–e** and **3c–e**. The ^{13}C NMR chemical shift values for the $W{=}C$ (approx. δ 257–259), $W{-}CO$, trans (approx. δ 202–203), and $W{-}CO$, cis (approx. δ 198–199) carbons in compounds **2a**, **c–e** and **3c–e** are similar to each other as well as to other (aminocarbene)tungsten complexes [5j,7a,10b,e–k]. Moreover, the mass spectra of complexes **2a**, **c–e** all exhibited parent molecular ions (M^+) along with ions for the successive loss of either one ($M^+ - CO$), two ($M^+ - 2CO$), three ($M^+ - 3CO$), four ($M^+ - 4CO$), or ($M^+ - 5CO$) carbon monoxide ligands. Similar mass spectral fragmentation patterns have been observed for other (aminocarbene)tungsten complexes [5a,7a,10g,i,j,l].

Although we have not extensively explored the synthetic potential of complexes **2**, it should be possible to prepare unsymmetrical (μ-bis(carbene))dimetal analogues of **3** from the reactions of **2** with different α-lithio (aminocarbene)metal anions of either tungsten or chromium. Furthermore, thermal or photochemical induced intramolecular carbene–carbene coupling [1a] of complexes **3** could lead to new 1,2-(dialkylamino)cycloalkene derivatives [13].

Experimental

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker WM-400 instrument at 400.1 and 100.6 MHz, respectively. ^1H NMR data are reported as follows: chemical shift in parts per million referenced to TMS (multiplicity, coupling constant(s) in hertz, number of protons). ^{13}C NMR data are reported as follows: chemical shift in parts per million referenced to residual solvent carbon resonances. Low-resolution mass spectra were acquired on a Finnigan 4000 instrument, and spectral data are listed as m/e (intensity of base peak) for only the tungsten-184 isotope. High-resolution mass spectra were obtained at the Midwest Center for Mass Spectroscopy, Department of Chemistry, University of Nebraska. Elemental analyses were performed by Microlytics, South Deerfield, MA. All reactions were conducted under an inert nitrogen or argon atmosphere. Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen. All reagents and starting materials were purchased from Aldrich Chemical Company. $(CO)_5W$-$[C(N(CH_3)_2)CH_3]$ (**1**) was prepared according to literature procedures [7a]. Flash chromatography [14] was conducted on E. Merck silica gel 60 (40–63 μm).

$(CO)_5W[C(N(CH_3)_2)(CH_2)_2I]$ (**2a**)

A THF solution (30 ml) of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (**1**) (0.50 g, 1.3 mmol), which had been cooled to −78°C, was treated with 0.61 ml (1.5 mmol) of 2.5 *M* ^nBuLi in hexane. The resulting solution was stirred at −78°C for 30 min, treated with diiodomethane (0.61 ml, 7.6 mmol), and then stirred for an additional 6 h. The solution was warmed to 25°C and the solvent removed under vacuum. The resulting residue was taken up in a minimum amount of methylene chloride and transferred to a column of silica gel. Eluting the column with 20% methylene chloride/80% hexane produced a yellow band which, upon collection of this band and removal of the solvent under vacuum, afforded recovered $(CO)_5W$ $[C(N(CH_3)_2)CH_3]$ (55 mg, 11%). Continued elution of the column with 20% methylene chloride/80% hexane produced a second yellow band which, upon collection of all the yellow fractions and removal of the solvent under vacuum, afforded complex **2a** (35 mg, 5%): yellow needles; m.p. 73–75°C. ^1H NMR ($CDCl_3$): δ 3.80 (s, 3H); 3.69 (t, $J = 9.8$ Hz, 2H); 3.35 (s, 3H); 3.16 (t, $J = 8.9$ Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 257.05, 202.44, 198.43, 57.91, 56.04, 41.81, 29.68. MS: *m/e* 535 (M^+, 40%), 507 (50), 451 (50), 423 (100), 395 (30). HRMS (^{184}W): Found: 534.9109. $C_{10}H_{10}INO_5W$ calc.: 534.9114. Anal. Found: C, 22.34; H, 1.76; N, 2.48. $C_{10}H_{10}INO_5W$ calc.: 22.45; H, 1.88; N, 2.62%.

$(CO)_5W[C(N(CH_3)_2)(CH_2)_4I]$ (**2c**)

A THF solution (50 ml) of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (**1**) (1.00 g, 2.5 mmol), which had been cooled to −78°C, was treated with 1.20 ml (3.0 mmol) of 2.5 *M* ^nBuLi in hexane. The resulting solution was stirred at −78°C for 30 min, treated with 1,3-diiodopropane (3.00 ml, 26.1 mmol), and then stirred for an additional 6 h. The solution was warmed to 25°C and the solvent removed under vacuum. The resulting residue was taken up in a minimum of hexane and transferred to a column of silica gel. Eluting the column with 20% methylene chloride/80% hexane and collection of all the yellow fractions, and then removal of the solvent under vacuum afforded **2c** (1.32 g, 93%): yellow crystals; m.p. 69°C. ^1H NMR ($CDCl_3$): δ 3.97 (s, 3H); 3.34 (s, 3H); 3.24 (t, $J = 6.7$ Hz, 2H); 3.15 (t, $J = 8.5$ Hz, 2H); 1.95 (p, $J = 7.0$ Hz, 2H); 1.56 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 258.35, 202.96, 198.89, 56.03, 52.58, 40.93, 32.80, 25.42, 6.10. MS: *m/e* 563 (M^+, 5%), 535 (10), 507 (5), 479 (0.6), 451 (0.8). Anal. Found: C, 25.60; H, 2.62; N, 2.46. $C_{12}H_{14}INO_5W$ calc.: C, 25.60; H, 2.51; N, 2.49%.

$(CO)_5W[C(N(CH_3)_2)(CH_2)_5I]$ (**2d**)

A THF solution (30 ml) of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (**1**) (0.50 g, 1.3 mmol), which was cooled to −78°C, was treated with 0.61 ml (1.5 mmol) of 2.5 *M* ^nBuLi in hexane. The resulting solution was stirred at −78°C for 30 min, treated with 1,4-diiodobutane (1.00 ml, 7.6 mmol) and then stirred for an additional 6 h. The solution was warmed to 25°C and the solvent removed under vacuum. The resulting residue was taken up in a minimum amount of methylene chloride and transferred to a column of silica gel. Eluting the column with 20% methylene chloride/80% hexane resulted in two yellow bands. Recovered **1** was obtained from the first band whereas collection of all the yellow fractions from the second band, and removal of the solvent under vacuum afforded **2d** (0.51 g, 69%): yellow oil. ^{1}H NMR ($CDCl_3$): δ 3.77 (s, 3H); 3.30 (s, 3H); 3.20 (t, $J = 6.9$ Hz, 2H); 3.13 (t, $J = 8.2$ Hz, 2H); 1.87 (p, $J = 7.2$ Hz, 2H); 1.54 (m, 2H); 1.45 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 258.40, 203.05, 198.90, 55.95, 53.66, 40.64, 32.90, 30.42, 23.79, 6.34. MS: *m/e* 577 (M^+, 30%), 549 (10), 521 (50), 465 (30), 437 (50). HRMS (^{182}W): Found: 574.9533. $C_{13}H_{16}INO_5W$ calc.: 574.9556. Anal. Found: C, 26.97; H, 2.83; N, 2.42. $C_{13}H_{16}INO_5W$ calc.: C, 27.06; H, 2.80; N, 2.43%.

$(CO)_5W[C(N(CH_3)_2)(CH_2)_6I]$ (2e)

A THF solution (30 ml) of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (**1**) (0.50 g, 1.3 mmol), which was cooled to −78°C, was treated with 0.61 ml (1.5 mmol) of 2.5 *M* ^{n}BuLi in hexane. The resulting solution was stirred at −78°C for 30 min, treated with 1,5-diiodopentane (1.13 ml, 7.6 mmol) and then stirred for an additional 6 h. The solution was warmed to 25°C and the solvent removed under vacuum. The resulting residue was taken up in a minimum amount of methylene chloride and transferred to a column of silica gel. Eluting the column with 25% methylene chloride/75% hexane and collection of all the second yellow fractions, and removal of the solvent under vacuum afforded **2e** (0.59 g, 79%): yellow oil. ^{1}H NMR ($CDCl_3$): δ 3.77 (s, 3H); 3.30 (s, 3H); 3.20 (t, $J = 6.9$ Hz, 2H); 3.12 (m, 2H); 1.84 (m, 2H); 1.46 (m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 258.49, 203.14, 198.91, 55.91, 53.80, 40.61, 33.07, 30.05, 28.51, 24.54, 6.85. MS: *m/e* 591 (M^+, 30%), 535 (50), 479 (20), 451 (40). HRMS (^{182}W): Found: 588.9708. $C_{14}H_{18}INO_5W$ calc.: 588.9713. Anal. Found: C, 28.35; H, 2.99; N, 2.36. $C_{14}H_{18}INO_5W$ calc.: C, 28.45; H, 3.07; N, 2.37%.

$(CO)_5W[C(N(CH_3)_2)(CH_2)_5C(N(CH_3)_2)]W(CO)_5$ (3c)

A THF solution (50 ml) of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (**1**) (0.80 g, 2.0 mmol), which had been cooled to −78°C, was treated with 0.96 ml (2.4 mmol) of 2.5 *M* ^{n}BuLi in hexane. The resulting solution was stirred at −78°C for 30 min and then a THF solution (50 ml) of **2c** (1.36 g, 2.4 mmol) was slowly introduced through a cannula. After the addition was complete the reaction mixture was warmed to 25°C with continued stirring for 24 h. The solvent was removed under vacuum and the resulting residue was taken up in a minimum amount of methylene chloride and transferred to a column of silica gel. Eluting the column with 25% methylene chloride/75% hexane initially produced a yellow band which, upon removal of the solvent under vacuum, gave recovered **2c** (0.39 g). Continued elution and collection of all the yellow fractions, and removal of the solvent under vacuum afforded **3c** (1.00 g, 61%): yellow plates; m.p. 132–134°C. ^{1}H NMR ($CDCl_3$): δ 3.78 (s, 6H); 3.30 (s, 6H); 3.14 (t, $J = 8.3$ Hz, 4H); 1.60–1.42 (m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 258.77, 202.96, 198.95, 55.99, 53.71, 40.69, 29.86, 24.73. Anal. Found: C, 30.21; H, 2.52; N, 3.33. $C_{21}H_{22}N_2O_{10}W_2$ calc.: C, 30.38; H, 2.67; N, 3.37%.

$(CO)_5W[C(N(CH_3)_2)(CH_2)_6C(N(CH_3)_2)]W(CO)_5$ (*3d*)

A THF solution (30 ml) of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (**1**) (0.50 g, 1.3 mmol), which had been cooled to −78°C, was treated with 0.61 ml (1.5 mmol) of 2.5 *M* ^{n}BuLi. The resulting solution was stirred at −78°C for 30 min and then a THF solution (50 ml) of **2d** (0.75 g, 1.3 mmol) was slowly introduced through a cannula. After the addition was complete the reaction mixture was warmed to 25°C with continued stirring for 24 h. The solvent was removed under vacuum and the resulting residue was taken up in a minimum amount of methylene chloride, and transferred to a column of silica gel. Eluting the column with 20% methylene chloride/80% hexane initially produced a yellow band which, upon removal of the solvent under vacuum, gave recovered **2d** (0.22 g). Continued elution and collection of all the yellow fractions, and removal of the solvent under vacuum afforded **3d** (0.64 g, 58%): yellow powder; m.p. 185°C (dec). ^{1}H NMR ($CDCl_3$): δ 3.78 (s, 6H); 3.30 (s, 6H); 3.13 (m, 4H); 1.47 (br m, 8H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 259.11, 202.96, 199.05, 56.00, 53.94, 40.67, 29.41, 24.73. Anal. Found: C, 31.20; H, 2.66; N, 3.29. $C_{22}H_{24}N_2O_{10}W_2$ calc.: C, 31.30; H, 2.87, N, 3.32%.

$(CO)_5W[C(N(CH_3)_2)(CH_2)_7C(N(CH_3)_2)]W(CO)_5$ (*3e*)

A THF solution (30 ml) of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (**1**) (0.50 g, 1.3 mmol), which had been cooled to −78°C, was treated with 0.61 ml (1.5 mmol) of 2.5 *M* ^{n}BuLi in hexane. The resulting solution was stirred at −78°C for 30 min and then a THF solution (50 ml) of **2e** (0.77 g, 1.3 mmol) was slowly introduced through a cannula. After the addition was complete the reaction mixture was warmed to 25°C with continued stirring for 24 h. The solvent was removed under vacuum and the resulting residue was taken up in a minimum amount of methylene chloride, and transferred to a column of silica gel. Eluting the column with 20% methylene chloride/80% hexane initially produced a yellow band which, upon removal of the solvent under vacuum, gave recovered **2e** (0.23 g). Continued elution and collection of all the yellow fractions, and removal of the solvent under vacuum afforded **3e** (0.58 g, 52%): yellow powder; m.p. 116–117°C. ^{1}H NMR ($CDCl_3$): δ 3.77 (s, 6H); 3.30 (s, 6H); 3.11 (m, 4H); 1.44 (br m, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 258.56, 203.19, 198.94, 55.90, 53.85, 40.55, 29.29, 28.84, 24.64. Anal. Found: C, 32.11, H, 2.95; N, 3.20. $C_{23}H_{26}N_2O_{10}W_2$ calc.: C, 32.19; H, 3.05; N, 3.27%.

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