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REGIOSELECTIVE ANION GENERATION AND ALKYLATION AT CARBON α TO NITROGEN IN $(CO)_5W{=}C[N(CH_3)_2]C_6H_4$-*p*-$CH_3$

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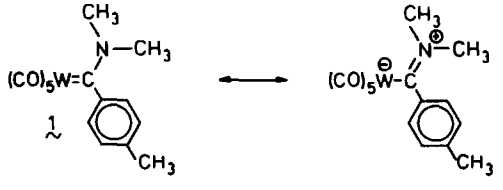
Summary

Treatment of $(CO)_5W{=}C[N(CH_3)_2]C_6H_4$-*p*-$CH_3$ (**1**) with lithium diisopropylamide (LDA) in THF at −78°C followed by quenching with D_2O leads to incorporation of deuterium into the (*E*)-*N*-methyl group only. Reaction of the anion of **1** with benzyl bromide at −78°C followed by quenching with water gave the *E*-isomer of $(CO)_5W{=}C[N(CH_3)CH_2CH_2C_6H_5]C_6H_4$-*p*-$CH_3$ (**2E**, 26%) and recovered **1**. When a mixture of the anion of **1** and benzyl bromide was warmed from −78°C to ambient temperature, a mixture of the *E*-isomer of the dibenzylated product $(CO)_5W{=}C[N(CH_3)CH(CH_2C_6H_5)_2]C_6H_4$-*p*-$CH_3$ (**4E**, 34%) and recovered starting material **1** was obtained. Reaction of the anion of **1** with allyl bromide gave $(CO)_5W{=}C[N(CH_3)CH_2CH_2CH{=}CH_2]C_6H_4$-*p*-$CH_3$ (**5**, 38%) and with methyl iodide gave a mixture of $(CO)_5W{=}C[N(CH_3)CH_2CH_3]C_6H_4$-*p*-$CH_3$ (**6**, 7%) and $(CO)_5W{=}C[N(CH_3)CH(CH_3)_2]C_6H_4$-*p*-$CH_3$ (**7**, 16%).

Introduction

A variety of activated amine derivatives [1] can be deprotonated α to the amine nitrogen with strong bases. The resulting anions can be reacted with electrophiles to yield substitution products. Thus nitrosoamines [2], hindered amides [3], and formamidines [4] can all be deprotonated to form α-amino carbanions and have been shown to be synthetically useful reagents. We recently discovered that amino substituted carbene complexes of tungsten can also be deprotonated α to nitrogen to form dipole-stabilized carbanions [5].



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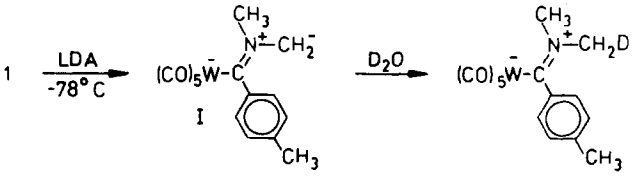
Complexes such as $(CO)_5W{=}C[(N(CH_3)_2]C_6H_4$-*p*-$CH_3$ (**1**) are stabilized by donation of the nitrogen lone pair electrons to the electropositive carbene carbon. The dipole structure is the major contributor to the resonance hybrid, giving rise to a partial carbon–nitrogen double bond. Because of hindered rotation about the partial carbon nitrogen double bond, complex **1** has two chemically distinct NCH_3 groups that give rise to separate ^1H NMR resonances at δ 3.03 for the *Z*- or *syn* NCH_3 group and at δ 1.89 for the *E*- or *anti* NCH_3 group. The rotational barrier about the carbon–nitrogen partial double bond in amino-substituted carbene complexes has been estimated to be > 30 kcal mol^{-1} [6]. Here we report that the *anti N*-methyl group of **1** can be deprotonated by strong bases and that the resulting dipole-stabilized carbanion can be trapped with electrophiles.

Results

Deprotonation of $(CO)_5W{=}C[(N(CH_3)_2]C_6H_4$-p-$CH_3$ (1)

When a yellow solution of **1** in THF was treated with three equivalents of lithium diisopropylamide (LDA) at $-78°C$, the solution became dark red within 5 min. After 1 h at $-78°C$, D_2O was added and the solution turned light orange. **1** was reisolated by thin layer chromatography with 67% recovery and was analyzed by ^1H and ^2H NMR and by MS.



In the ^1H NMR, the integrated ratio of the (*E*)-NCH_3 resonance at δ 1.89 to the (*Z*)-NCH_3 resonance at δ 3.03 to the tolyl methyl resonance at δ 2.01 was 2.0/3.0/3.0. This indicates incorporation of 100% of one deuterium exclusively in the (*E*)-NCH_3 group. ^2H NMR confirmed that deuterium was incorporated only ($> 95\%$) at the (*E*)-NCH_3 group.

The assignment of the resonance at δ 1.89 to the (*E*)-NCH_3 group is unambiguous. Fischer's [7] initial assignments of the chemical shifts of the (*Z*)- and (*E*)-NCH_3 resonances were confirmed by us for several cases where interconversion between *Z* isomers and chelated metal-carbene-alkene complexes allowed definitive assignments [5,8].

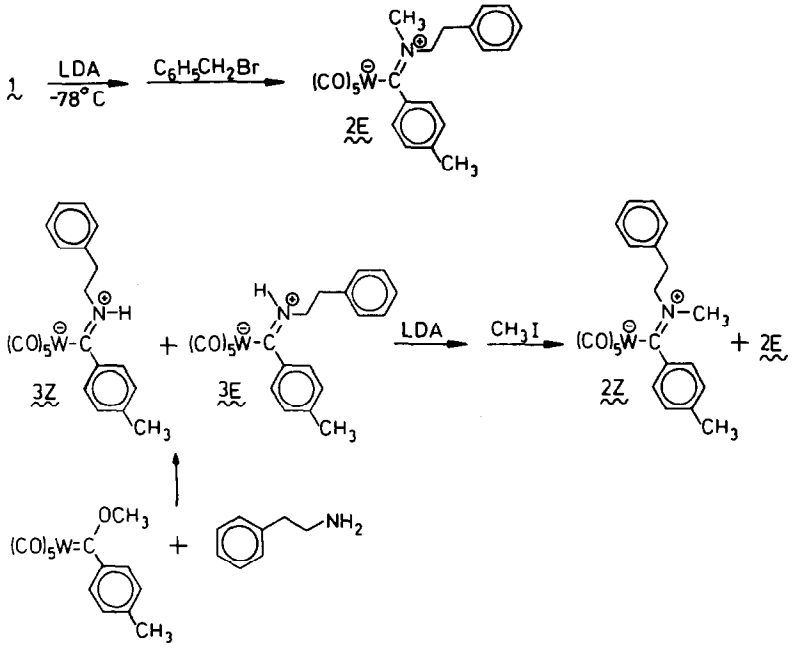
The mass spectrum of recovered **1** indicated a ratio of 44/12/43 of $d_0/d_1/d_2$ material. The total deuterium content of 98% is in agreement with the 100% found by NMR. The extensive amount of d_2 material indicated substantial exchange during the quench. When CH_3OD was used to quench the anion of **1**, NMR showed 0.60 deuterium per tungsten and MS again showed extensive d_2 formation ($0.61d_0/0.18d_1/0.19d_2$).

The use of a very strong base such as LDA is required for these deprotonations. When less than 3 equiv. of LDA was used lower incorporation of deuterium was observed after a D_2O quench. No deprotonation of **1** was seen using lithium hexamethyldisilazide in THF at -78 to $20°C$. No deuterium exchange was observed when a THF solution of **1** was stirred either with KOD and D_2O or with CH_3OK

and CH_3OD. When deprotonation of **1** with n-BuLi or t-BuLi was attempted in THF at −78°C followed by a CH_3OD quench, some incorporation of deuterium into **1** was seen but < 40% **1** was recovered.

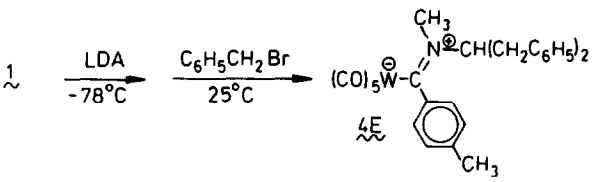
Alkylation of the anion of 1

Alkylation of the anion of **1** with benzyl bromide or allyl bromide at low temperature led to the isolation of monoalkylated products and of recovered starting material in comparable amounts. For example, when the anion of **1** (generated by treatment with 3 equiv. of LDA for 1 h at −78°C) was stirred with 10 equiv. of benzyl bromide in THF at −78°C for 6 h and the reaction mixture quenched by addition of water at −78°C, the monobenzylated product **2E** was isolated in 26% yield and **1** was recovered in 58% yield after thin layer chromatography.



The configuration of **2E** was assigned on the basis of the ^1H NMR chemical shifts of the alkyl groups attached to nitrogen. In **2E**, the NCH_3 group appears at δ 3.18 as expected for a methyl group *syn* to tungsten and the NCH_2 group appears at δ 2.82. To confirm this assignment, a mixture of the two configurational isomers **2E** and **2Z** was synthesized. Reaction of phenethylamine with $(CO)_5W{=}C(OCH_3)C_6H_4$-*p*-CH_3 gave a 2/1 mixture of **3Z** and **3E**, $(CO)_5W{=}C(NHCH_2CH_2C_6H_5)C_6H_4$-*p*-$CH_3$. Deprotonation of the NH functions of this mixture with LDA and alkylation at nitrogen with methyl iodide gave a 3/1 mixture of **2Z** and **2E** which was isolated by column chromatography. In addition to resonances seen for **2E**, the ^1H NMR spectrum of the mixture had resonances at δ 2.07 for the NCH_3 group and at δ 4.00 for the NCH_2 group of **2Z**. Thus the NCH_3 group *syn* to tungsten in **2E** is 1.11 ppm downfield of the NCH_3 group *anti* to tungsten in **2Z** and the NCH_2 group *syn* to tungsten in **2Z** is 1.18 ppm downfield of the NCH_3 group in **2E**.

The monobenzylation of the anion of **1** occurred with complete regioselectivity; no **2Z** was observed in the reaction mixture.



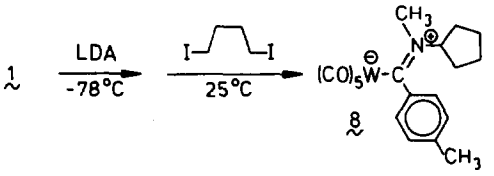
In an attempt to obtain a higher conversion to monoalkylated product **2E**, the reaction mixture containing the anion of **1** and excess benzyl bromide was warmed from −78°C to ambient temperature before quenching with water. Surprisingly, none (< 2%) of the monobenzylated product **2E** was obtained. Instead, thin layer chromatography led to the isolation of dibenzylated product **4E** in 34% yield and to 32% recovery of starting material **1**. In **4E**, both benzyl groups were introduced regioselectively at the carbon *anti* to tungsten. The chemical shift of the NCH_3 group of **4E** at δ 3.40 establishes that the methyl group is *syn* to tungsten. The diastereotopic benzylic protons of **4E** are coupled to a single methine hydrogen and appear as the AB portion of an ABX multiplet with J_{AB} 13.8, J_{AX} 9.0, J_{BX} 5.2 Hz, ν_A 2.28, and ν_B 2.13 ppm.

In an attempt to determine why only dibenzylated product **4E** and starting material were obtained in the above reaction, the reaction mixture was quenched with CH_3OD at −78°C. Thin layer chromatography gave 31% recovered starting material **1** and 25% monobenzylated **3E**. The ^1H NMR spectrum of **3E** indicated nearly complete (> 85%) monodeuteration at the NCHD group. The NCHD group appears as a sharp triplet at δ 2.84 and the benzylic protons of the $NCHDCH_2C_6H_5$ unit appear as a sharp doublet at δ 2.11. The ^1H NMR of recovered **1** indicated about 10% deuterium incorporation into the NCH_3 group *anti* to tungsten.

These results give excellent evidence that the initially formed monobenzylated material **2E** reacts with the anion of **1** to generate the anion of **2E** and neutral **1**. The low yield of **2E** and the extensive recovery of **1** after protonation at −78°C is readily understood in these terms. Apparently, the second benzylation step is slow at −78°C and occurs only upon warming to room temperature. We do not understand why the anion of **2E** and neutral **1** are strongly favored at equilibrium.

Alkylations of the anion of **1** with allyl bromide or methyl iodide also proceeded in low to moderate yield and were accompanied by extensive recovery of starting material. Reaction of the anion of **1** with 10 equiv. of allyl bromide at −78°C followed by quenching with H_2O at −78°C led to the formation of monoallylated **5** in 38% isolated yield and to recovery of 42% of starting material **1**. Alkylation again occurred only at the *E*-methyl group as shown by ^1H NMR. When the reaction was warmed to room temperature before quenching with H_2O, some diallylated product was observed in addition to **5** and recovered **1**. An attempt was made to circumvent the problem of protonation of the anion of **1** by the monoalkylated product by performing an inverse addition of the carbanion of **1** to a THF solution of allyl bromide at −78°C over a period of 45 min followed immediately by a water quench at −78°C. However, this led to a lower yield of monoallylated **5** (15%) and recovered starting material (35%).

A solution of the anion of **1** and CH_3I was warmed from −78°C to room temperature and quenched with H_2O after 20 h. This layer chromatography led to the isolation of 7% monomethylated **6**, 16% dimethylated **7**, and 45% recovered **1**. ^1H NMR demonstrated that methylation had occurred only at *E*-methyl group.



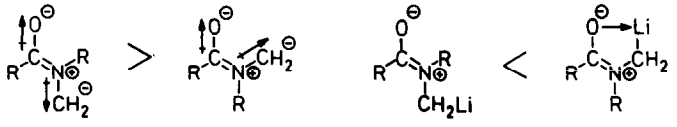
We attempted to take advantage of the relatively more efficient second alkylation step by examining the reaction of the anion of **1** with 1,4-diiodobutane. A solution containing the anion of **1** (generated with 3 equiv. of LDA) and a ten-fold excess of 1,4-diiodobutane was warmed from −78°C to room temperature and stirred for 8 h. Dialkylation at the *E*-methyl group generated the cyclopentane ring of **8** which was isolated in 17% yield by thin layer chromatography.

Several attempts were made under various conditions to trap the carbanion of **1** with benzaldehyde. Neither products of condensation nor condensation followed by dehydration were seen. Work-up of the reaction mixtures led to the recovery of about 50% of starting material **1**. Reaction of the carbanion of **1** with a Lewis acid complex of benzaldehyde and $BF_3 \cdot OEt_2$ also failed to yield condensation products.

Since no trialkylation products have been observed, it was thought that reaction at a secondary center might proceed more cleanly. However, when the pyrrolidine complex $(CO)_5W{=}C(\overline{NCH_2CH_2CH_2CH_2})(C_6H_4\text{-}p\text{-}CH_3)$ (**9**) was treated with three equivalents of LDA at −78°C and the reaction quenched with CH_3OD little incorporation of deuterium was observed (< 10%). Warming the reaction to room temperature before quenching with CH_3OD led to a low recovery of the pyrrolidine complex (42%) and again little deuterium incorporation.

Discussion

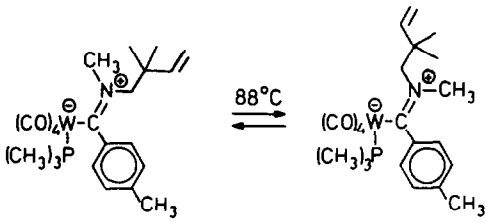
The deprotonation of **1** occurs with high regioselectivity at the NCH_3 group *anti* to tungsten. The major resonance contributor to the structure of this anion is I in which the negatively charged CH_2 and $W(CO)_5$ units are separated by a larger distance that they would be for the anion formed by deprotonation of the NCH_3 group *syn* to tungsten.



Calculations on the anions of amides show that the anion *anti* to oxygen is favored over the anion *syn* to oxygen because this provides the best orientation of the dipoles [9]. However, alkylation reactions of amides occur selectively at the *N*-alkyl group *syn* to oxygen [9,10]. This has been attributed to selective stabilization of the *syn* anion by chelation to a metal ion. Similar chelation stabilization is probably responsible for selective *syn* alkylation and *syn* deuterium exchange of formamidines [4] and *N*-nitrosoamines [11]. In the case of the anion of **1**, chelation to tungsten is unfavorable because tungsten is already six-coordinate and the negative charge is delocalized over the five carbonyl ligands. In the absence of chelation stabilization, the electronic preference for maximum separation of the negative ends of the dipoles is responsible for selective formation of the anion at the

NCH_3 group *anti* to tungsten.

It is unlikely that the *anti* regioselectivity of anion formation is due to steric effects since there is little steric difference between the *syn* and *anti* sites in arylaminocarbene complexes of tungsten. The reaction of primary amines with $(CO)_5W{=}C(OCH_3)C_6H_4$-*p*-CH_3 leads to a kinetically determined preferential formation (2/1 for **3Z** and **3E**) of the (*Z*)-*N*-alkyl isomer of $(CO)_5W{=}C(NHR)C_6H_4$-*p*-CH_3. The photostationary state for $(CO)_5W{=}C[N(CH_3)(CH_2CMe_2CH{=}CH_2)]C_6H_4$-*p*-$CH_3$ consisted of a 1.3/1.0 preference for the *Z* isomer in which the larger *N*-alkyl group is *syn* to tungsten [5]. Equilibration of $(CO)_4(PMe_3)W{=}C[N(CH_3)(CH_2CMe_2CH{=}CH_2)]C_6H_4$-*p*-$CH_3$ gave a 1/1 mixture of *Z* and *E* isomers [5].



The alkylation reactions of the anion of **1** were plagued by low yields of monoalkylation product and extensive recovery of starting material. This is due to a rapid deprotonation of the monoalkylation product by the anion of **1** which produces starting material **1** and the anion of the monoalkylation product. When the reaction mixture from the benzylation of the anion of **1** was quenched with D_2O, undeuterated **1** was recovered and the monobenzylated product **2E** was found to be monodeuterated. When the reaction mixture was warmed to room temperature, alkylation of the anion of the monobenzylated compound **2E** occurred to produce dibenzylated product **4E** which was isolated along with recovered starting material **1**. Apparently, there is a substantial thermodynamical preference for the more substituted anion. The more substituted anion is kinetically less reactive and requires warming to room temperature to achieve alkylation.

We have established that anions can be generated regioselectively at the (*E*)-*N*-alkyl group of amino carbene complexes. To take full advantage of this type of reactive intermediate, a better reagent than **1** is clearly needed. We are continuing to search for an amino carbene complex that can be cleanly monoalkylated at the carbon α to the amine nitrogen.

Experimental

General

All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. Tetrahydrofuran and diethyl ether were distilled from sodium and benzophenone prior to use. Hexane was distilled prior to use. CD_3CN was distilled from P_2O_5 then CaH_2. Diisopropylamine was distilled from KOH. Allyl bromide and benzyl bromide were washed with saturated $NaHCO_3$ then distilled water, dried over $MgSO_4$, and distilled. Iodomethane was distilled from P_2O_5 and stored over molecular sieves and mercury. Preparative thin layer chromatography was performed using Davison Davisil 62 silica gel.

For all reactions, lithium diisopropylamide (LDA) was prepared immediately prior to use by the following procedure: n-BuLi (1.39 *M* is hexane) was added by syringe to a stirred solution of 1 equiv. of diisopropylamine in THF at −78°C. The solution was then warmed to 0°C and stirred 10 min before use.

^{1}H NMR spectra were obtained on a Bruker WP-200 or WP-270 spectrometer. When quantitative results were required, a 30 s pulse delay was used between scans to minimize the effects of different relaxation times. ^{2}H NMR spectra were obtained on a JEOL FX-200 spectrometer. ^{13}C NMR were obtained on a JEOL FX-200 or a Bruker AM-500 spectrometer. Mass spectra were obtained on an AEI-MS-902 or a Kratos MS-80 spectrometer. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were obtained on a Beckman IR-4230 spectrophotometer. Analyses were performed by Schwarzkopf Microanalytical Labs.

Generation and D_2O quench of the anion of 1

A solution of LDA (1.29 mmol) in 20 ml THF was added to a solution of **1** in 20 ml THF at −78°C. After 1 h, 1 ml D_2O was added and the reaction mixture was warmed to room temperature. The solvent was evaporated and **1** was reisolated by preparative TLC (0.134 g, 67%).

Partial ^{1}H NMR (200 MHz, C_6D_6): δ 1.89 (2.0 H, (*E*)-NCH_3), 2.01 (3.0H, Ar-CH_3), 3.03 (3.0H, (*Z*)-NCH_3). ^{2}H NMR (30.6 MHz, C_6H_6): δ 1.95 (s, (*E*)-NCH_3).

MS: *m/e* (%): M^+: 475 (9.5), 474 (7.0), 473 (18.5), 472 (9.3), 471 (16.7), 470 (8.2), 469 (7.7). $M - CO^+$: 447 (15.7), 446 (10.0), 445 (29.2), 442 (15.3), 441 (11.7). $M - 3(CO)^+$: 392 (6.5), 391 (45.3), 390 (27.7), 389 (93.4), 388 (51.7), 387 (100), 386 (42.7), 385 (40.8).

The MS data was analyzed by a least-squares fit of the observed intensities of the most intense $M - 3(CO)^+$ envelope to a linear combination of predicted intensities for d_0, d_1, d_2, and d_3 material. The predicted values were obtained from a high resolution mass spectrum of **1**: *m/e* (%): $M - 3(CO)^+$: 392 (0), 391 (3.2), 390 (10.0), 389 (86.3), 388 (15.4), 387 (100), 386 (68.9), 385 (80.3). The intensities for the deuterated species were predicted by successively shifting this pattern up one mass unit for the incorporation of each deuterium. Least-squares analysis yields a ratio of 44/12/43/2 for $d_0/d_1/d_2/d_3$ material.

Pentacarbonyl[(E)-(N-methyl-N-2-phenylethylamino)(p-tolyl)carbene]tungsten(0) (2E)

A solution of LDA (1.50 mmol) in 20 ml THF was added to a stirred solution of **1** (0.250 g, 0.53 mmol) in 40 ml THF at −78°C. After 1 h, benzyl bromide (0.63 ml, 5.3 mmol) in 5 ml THF was added. The reaction mixture was stirred 6 h at −78°C and then quenched by addition of 0.5 ml H_2O at −78°C. The solution was warmed to room temperature and 40 ml ether and 40 ml water were added. The aqueous layer was washed with ether (2 × 10 ml). The combined ether extracts were dried ($MgSO_4$) and ether was evaporated. The orange residue was chromatographed on a short plug of silica gel (15 g). After elution of benzyl bromide with hexane, the mixture of carbene complexes was eluted with ether. Preparative TLC (SiO_2, 4/1 hexane/ether) followed by trituration of the resulting oils with hexane yielded **1** (0.146 g, 58%, $R_f = 0.26$) as a yellow solid and **2E** (0.077 g, 26%, $R_f = 0.39$) as a yellow solid, m.p. 90–92°C.

^{1}H NMR (270 MHz, C_6D_6) δ 2.00 (s, $ArCH_3$), 2.08 (t, *J* 7.5 Hz, CH_2Ph), 2.82 (t, *J* 7.1 Hz, NCH_2), 3.18 (s, NCH_3), 6.11 (d, *J* 7.7 Hz, 2 H, C_6H_4), 6.56

(m, 2H, C_6H_5), 6.83 (d, *J* 7.7 Hz, 2H, C_6H_4), 7.02 (m, 3H, C_6H_5). $^{13}C\{^1H\}$ NMR (50.1 MHz, CD_3CN, 0.07 *M* Cr(acac)$_3$) δ 21.0 ($ArCH_3$); 34.8 (CH_2Ph); 52.4 (NCH_3); 58.9 (NCH_2); 120.6, 129.3, 129.6 (*ortho, meta* C_6H_4 and C_6H_5); 127.7 (*para* C_6H_5); 136.4, 138.5, 151.2 (*ipso, para* C_6H_4, *ipso* C_6H_5); 199.4 (*cis* CO) 205.5 (*trans* CO); 256.8 (W=C). IR (hexane) 2060m, 1973w, 1938vs, 1933sh cm^{-1}.

Anal. Found: C, 47.08; H, 3.72. $C_{22}H_{19}NO_5W$ calcd.: C, 47.01; H, 3.42%.

Pentacarbonyl[(N-2-phenylethylamino)(p-tolyl)carbene]tungsten(0) (3E and 3Z)

2-Phenylethylamine (2.0 ml, 15 mmol) was added to $(CO)_5W{=}C(OCH_3)(C_6H_4$-*p*-$CH_3)$(2.0 g, 4.4 mmol) in 100 ml diethyl ether at 0°C. The color of the solution immediately changed from red to yellow. After 20 min at ambient temperature, the ether solution was washed with 100 ml of 1 *N* HCl, and then 100 ml saturated $NaHCO_3$, and dried ($MgSO_4$). Evaporation of ether gave a 2/1 mixture of **3Z** and **3E** as a yellow oil (1.71 g, 72%).

^1H NMR (C_6D_6, 270 MHz) δ 1.91 (t, *J* 6.7 Hz, CH_2Ph, **3Z**); 1.98 (s, $ArCH_3$, **3E** and **3Z**); 2.36 (t, *J* 7.1 Hz, CH_2Ph, **3E**); 2.53 (q, *J* 6.5 Hz, NCH_2, **3E**); 3.67 (q, *J* 7.1 Hz, NCH_2, **3Z**); 6.25 (d, *J* 8.1 Hz); 6.67 (m), 6.80 (d, *J* 7.2 Hz), 6.88 (d, *J* 8.1 Hz), 7.0–7.15 (m), 7.38–7.48 (bs, NH, **3Z**); 8.2–8.3 (bs, NH, **3E**). $^{13}C\{^1H\}$ NMR (50.1 MHz, CD_3CN, 0.07 *M* Cr (acac)$_3$) δ 19.9 ($ArCH_3$); 34.3 (CH_2Ph); 51.3 (NCH_2, **3E**); 56.4 (NCH_2, **3Z**); 119.9, 122.1, 126.4, 128.3, 135.8, 137.4, 147.2, 152.1 (aromatic); 198.1 (*cis* CO); 203.6 (*trans* CO, **3Z**); 203.9 (*trans* CO, **3E**); 255.6 (W=C, **3Z**); 253.7 (W=C, **3E**). IR (hexane) 2060m, 1966m, 1931vs, 1925sh cm^{-1}. HRMS: found: 547.0609. $^{184}WC_{21}H_{17}NO_5$ calcd.: 547.0612.

Pentacarbonyl[(N-methyl-N-2-phenylethylamino)(p-tolyl)carbene]tungsten(0) (2E and 2Z)

A solution of LDA (1.5 mmol) in 15 ml THF was added to **3Z** and **3E** (2/1, 0.75 g, 1.4 mmol) in 40 ml THF at −78°C. The reaction mixture was warmed to room temperature and recooled to −78°C. CH_3I (0.11 ml, 1.8 mmol) was added and the reaction mixture was warmed to room temperature. After 1 h, the solvent was evaporated and the residual yellow oil was chromatographed (15 g SiO_2, 95/5 hexane/ether) to yield a 3/1 mixture of **2Z** and **2E** as a yellow solid (0.61 g, 78%).

For **2Z** (determined as a mixture with **2E**): ^1H NMR (270 MHz, C_6D_6) δ 2.06 (s, $ArCH_3$), 2.07 (s, NCH_3), 2.74 (m, CH_2Ph), 4.00 (m, NCH_2), 6.39 (d, *J* 8.2 Hz, 2H, C_6H_4), 6.92 (d, *J* 8.2 Hz, 2H, C_6H_4), 7.0–7.3 (m, C_6H_5). $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_3CN, 0.07 *M* Cr(acac)$_3$) δ 20.7 ($ArCH_3$); 34.1 (CH_2Ph); 42.4 (NCH_3); 67.4 (NCH_2); 119.7, 129.1, 127.4, 129.3 (C_6H_4, C_6H_5); 135.9, 138.0, 151.8 (*ipso, para*, C_6H_4, *ipso* C_6H_5); 198.3 (*cis* CO, $J(^{183}W^{13}C)$ 127 Hz); 204.6 (*trans* CO); 253.1 (W=C). HRMS: found: 561.0765. $^{184}WC_{22}H_{19}NO_5$: calcd.: 561.0768.

Pentacarbonyl[(E)-N-methyl-N-(1-benzyl-2-phenylethyl)amino)(p-tolyl)carbene]tungsten(0) (4E)

LDA (1.91 mmol) in 25 ml THF was added to **1** (0.300 g, 0.64 mmol) in 50 ml THF at −78°C. After 1 h, benzyl bromide (0.76 ml, 6.4 mmol) in 10 ml THF was added at −78°C. The solution was stirred at room temperature for 22 h. THF was evaporated and 40 ml ether and 40 ml water were added. The aqueous phase was washed with ether (2 × 10 ml). The combined ether extracts were dried ($MgSO_4$) and evaporated. The residue was chromatographed (15 g, SiO_2). After elution of benzyl

bromide with hexane, the mixture of carbene complexes was eluted with ether. Preparative TLC (SiO_2, 4/1 hexane/ether) yielded **1** (0.097 g, 32%, $R_f = 0.32$) and **4E** (0.140 g, 34%, $R_f = 0.51$) m.p. 118–120°C (dec.), both as yellow solids after trituration with hexane.

^{1}H NMR (270 MHz, C_6D_6) δ 1.99 (s, $ArCH_3$); 2.13, 2.28 (AB of ABX pattern, J_{AB} 13.8, J_{AX}, J_{BX} 8.9, 5.2 Hz, $NCH(CH_2Ph)_2$); 3.40 (s, NCH_3); 4.01 (m, $NCH(CH_2Ph)_2$); 5.37 (d, J 7.5 Hz, C_6H_4); 6.61 (m, C_6H_5); 6.69 (d, J 7.5 Hz, C_6H_4); 7.08 (m, C_6H_5). ^{13}C {^{1}H} NMR (50.1 MHz, CD_3CN, 0.07 *M* $Cr(acac)_3$) δ 21.1 ($ArCH_3$); 39.1 (CH_2Ph); 47.2 (NCH_3); 70.6 (NCH); 120.8, 128.1, 128.7, 129.7, 130.4 (*ortho, meta* C_6H_4, C_6H_5); 135.9, 150.5 (C_6H_4 *ipso, para*); 138.3 (C_6H_5 *ipso*); 199.4 (*cis* CO); 205.9 (*trans* CO); 260.2 (W=C). IR (hexane) 2060m, 1975w, 1940vs, 1930sh cm^{-1}. HRMS found: 651.1237. $^{184}WC_{29}H_{25}NO_5$ calcd.: 651.1236.

Generation and CH_3OD quench of the anion of 2E

A solution of LDA (0.63 mmol) in 20 ml THF was added to a stirred solution of **1** (0.100 g, 0.21 mmol) in 25 ml THF at −78°C. After 1 h, benzyl bromide (0.25 ml, 2.1 mmol) in 5 ml THF was added. After 6 h at −78°C, 0.5 ml CH_3OD was added and the solution was warmed to room temperature. SiO_2 (0.5 g) was added and the solvent was evaporated. The benzyl bromide was eluted by column chromatography (SiO_2, 15 g) with hexane then the mixture of carbene complexes was eluted with ether. Preparative TLC (SiO_2, 4/1 hexane/ether) yielded **1** (0.031 g, 31%) and **2E** (0.029 g, 25%).

For recovered **1**: Partial ^{1}H NMR (C_6D_6, 270 MHz) δ 1.89 (2.9 H, (*E*)-NCH_3), 2.01 (3.0H, $ArCH_3$), 3.03 (3.0H, (*Z*)-NCH_3).

For **2E**: Partial ^{1}H NMR (C_6D_6, 270 MHz) δ 2.01 (s, 3.0H, $ArCH_3$), 2.12 (d, J 7.4 Hz, 2.0H, CH_2Ph), 2.84 (t, J 7.5 Hz, 2.15 H, NCHD); 3.22 (s, 3.0H, NCH_3).

Pentacarbonyl[(E)-(N-methyl-N-3-butenylamino)(p-tolyl)carbene]tungsten(0) (5)

LDA (1.3 mmol) in 15 ml THF was added to **1** (0.200 g, 0.42 mmol) in 40 ml THF at −78°C. After 1 h at −78°C, allyl bromide (0.36 ml, 4.3 mmol) was added. After 6 h, 0.5 ml water was added at −78°C and the solution was warmed to room temperature. The THF and excess allyl bromide were evaporated under vacuum and 25 ml ether and 25 ml water were added. The aqueous phase was separated and washed with ether (2 × 10 ml). Preparative TLC (SiO_2, 4/1 hexane/ether) of the concentrated ether extracts afforded **1** (0.084 g, 42%, $R_f = 0.29$) and **5** (0.081 g, 38%, $R_f = 0.43$) as a yellow oil.

^{1}H NMR (200 MHz, C_6D_6) δ 1.53 (q, J 7.3 Hz, $CH_2CH{=}CH_2$), 2.00 (s, $ArCH_3$), 2.64 (t, J 7.5 Hz, NCH_2), 3.15 (s, NCH_3), 4.64 (dd, J 16.8, 1.6 Hz, CH=CHH), 4.75 (dd, J 10.0, 1.6 Hz, CH=CHH); 5.00 (m, $CH{=}CH_2$), 6.42 (d, J 8.2 Hz, 2H, C_6H_4), 6.86 (d, J 8.2 Hz, 2H, C_6H_4). ^{13}C {^{1}H} NMR (50.1 MHz, CD_3CN, 0.07 *M* $Cr(acac)_3$) δ 21.2 ($ArCH_3$); 33.3 ($CH_2CH{=}CH_2$); 52.5 (NCH_3); 57.0 (NCH_2); 120.1, 129.6 (*ortho, meta*); 135.1, 136.7, 151.5 (*ipso, para*, $CH{=}CH_2$); 199.7 (*cis* CO); 205.8 (*trans* CO); 356.4 (W=C); $CH{=}CH_2$ not seen. IR (hexane) 2064m, 1974w, 1938vs, 1933sh cm^{-1}. HRMS found: 511.0616. $^{184}WC_{18}H_{17}NO_5$ calcd. 511.0612.

Pentacarbonyl[(E)-(N-methyl-N-ethylamino)(p-tolyl)carbene]tungsten(0) (6) and pentacarbonyl[(E)-(N-methyl-N-isopropylamino)(p-tolyl)carbene]tungsten(0) (7)

LDA (1.3 mmol) in 15 ml THF was added to **1** (0.200 g, 0.42 mmol) in 40 ml

THF at −78°C. After 1 h, CH_3I (0.26 ml, 4.2 mmol) was added at −78°C. After 20 h at ambient temperature, THF and excess CH_3I were evaporated and 25 ml ether and 25 ml water were added. The aqueous phase was separated and washed with ether (2 × 10 ml). Preparative TLC (SiO_2, 9/1 hexane/ether, 3 elutions) of the concentrated ether extracts afforded three bands: **6**, (0.015 g, 7%) as a yellow solid, m.p. 90–92°C; **7** (0.033 g, 16%) as a yellow solid, m.p. 69–72°C; and **1** (0.089 g, 45%).

For 6. ^1H NMR (270 MHz, C_6D_6) δ 0.30 (t, J 7.1 Hz, NCH_2CH_3), 2.01 (s, $ArCH_3$), 2.50 (q, J 7.3 Hz, NCH_2CH_3), 3.13 (s, NCH_3), 6.40 (d, J 8.0 Hz, 2H, C_6H_4) 6.89 (d, J 7.7 Hz, 2H, C_6H_4). IR (hexane) 2055m, 1959w, 1923vs, 1920sh cm^{-1}. HRMS found: 485.0461. $^{184}WC_{16}H_{15}NO_5$ calcd.: 485.0456.

For 7. ^1H NMR (270 MHz, C_6D_6) δ 0.39 (d, J 6.8 Hz, $NCH(CH_3)_2$), 2.08 (s, $ArCH_3$), 3.18 (s, NCH_3), 3.83 (m, J 8.0 Hz, $NCH(CH_3)_2$), 6.50 (d, J 8.0 Hz, 2H, C_6H_4); 7.05 (d, J 8.0 Hz, 2H, C_6H_4). IR (hexane) 2050m, 1955w, 1924vs, 1915sh cm^{-1}. HRMS found: 499.0609. $^{184}WC_{17}H_{17}NO_5$ calcd.: 499.0612.

*Pentacarbonyl[(E)-N-methyl-N-cyclopentylamino)(p-tolyl)carbene]tungsten(0) (**8**)*

LDA (2.2 mmol) in 30 ml THF was added to **1** (0.350 g, 0.74 mmol) in 50 ml THF at −78°C. After 1 h, 1,4-diiodobutane (0.9 ml, 7.4 mmol) was added at −78°C. After 8 h at ambient temperature, 0.5 ml H_2O and ~ 0.5 g SiO_2 were added and solvent was evaporated. Column chromatography (15 g SiO_2) with hexane eluted unreacted diiodobutane. Then, elution with ether gave a yellow band which was further purified by preparative TLC (SiO_2, 4/1 hexane/ether) to yield **8** (0.067 g, 17%, $R_f = 0.74$) and **1** (0.142 g, 40%, $R_f = 0.36$) as yellow solids.

^1H NMR (200 MHz, C_6D_6) δ 0.65–0.85 (m, 2H), 0.90–1.18 (m, 6H), 2.01 (s, $ArCH_3$); 3.15 (s, NCH_3); 3.86–4.02 (m, NCH); 6.47 (d, J 7.9 Hz, 2H, C_6H_4); 6.90 (d, J 7.9 Hz, 2H, C_6H_4). ^{13}C {^1H} NMR (50.1 MHz, CD_3CN, 0.07 M $Cr(acac)_3$) δ 21.0 ($ArCH_3$); 25.4, 30.8 (ring CH_2); 47.0 (NCH_3); 66.8 (NCH); 120.4, 129.6 (*ortho, meta*); 136.3, 152.0 (*ipso, para*); 199.7 (*cis* CO); 205.6 (*trans* CO); 256.2 (W=C). IR (hexane) 2060m, 1973w, 1937vs, 1930sh cm^{-1}. HRMS found: 525.0787. $^{184}WC_{19}H_{19}NO_5$ calcd.: 525.0768.

*Pentacarbonyl[pyrrolidino)(p-tolyl)carbene]tungsten(0) (**9**)*

Pyrrolidine (0.90 ml, 10.78 mmol) was added to $(CO)_5W{=}C(OCH_3)(C_6H_4)p$-$CH_3$) (3.50 g, 7.64 mmol) in 250 ml of diethyl ether at 0°C. After 20 min, ether was evaporated and the resulting yellow oil was recrystallized from hexane to give **9** (2.85 g, 75%) as a yellow solid, m.p. 101–103°C.

^1H NMR (200 MHz, C_6D_6) δ 0.90 (m, (*E*)-NCH_2CH_2), 1.07 (m, (*Z*)-NCH_2CH_2), 2.08 (s, $ArCH_3$), 2.43 (t, J 7.1 Hz, *E*-NCH_2CH_2), 3.71 (t, J 7.1 Hz, (*Z*)-NCH_2CH_2), 6.42 (d, J 8.4 Hz, 2H, C_6H_4), 6.92 (d, J 8.4 Hz, 2H, C_6H_4). ^{13}C {^1H} NMR (50.1 MHz, CD_3CN, 0.07 M $Cr(acac)_3$) δ 21.0 ($ArCH_3$); 25.5, 26.1 (CH_2CH_2); 55.4 ((*E*)-NCH_2); 63.1 ((*Z*)-NCH_2); 120.2, 129.7 (*ortho, meta*); 136.4, 153.0 (*ipso, para*); 199.7 (*cis* CO); 205.3 (*trans* CO); 248.5 (W=C). IR (hexane) 2055m, 1976w, 1938vs, 1932sh cm^{-1}. HRMS found: 497.0470. $^{184}WC_{17}H_{15}NO_5$ calcd.: 497.0456.

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