ORGANOMETALLICS

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Organometallics, **1994**, 13 (12), 4676-4678• DOI: 10.1021/om00024a010 • Publication Date (Web): 01 May 2002

4676 *Organometallics* **1994**, *13*, 4676−4678

Inter- and Intramolecular Oxidative Coupling of Manganese Carbene Anions in the Presence of Copper Salts. Synthesis of (μ-Bis(carbene))dimanganese Complexes

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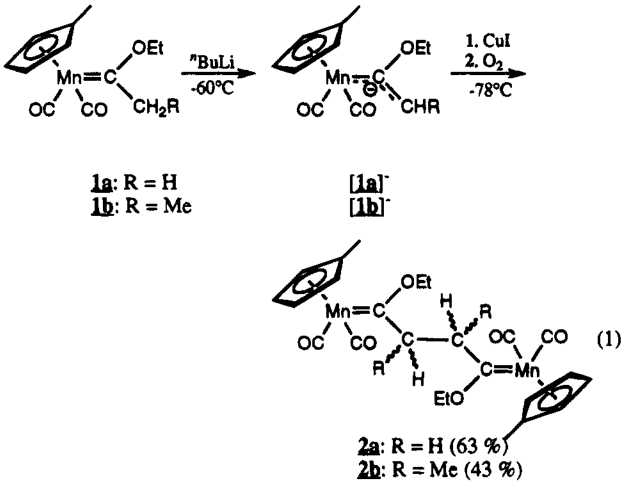
Received August 17, 1994⊗

Summary: The carbene anions resulting from in situ deprotonation of the "Fischer-type" carbene complexes $Cp'(CO)_2Mn{=}C(OEt)CH_2R$ *(R = H, Me) and* $Cp'(CO)_2Mn{=}\overline{CN(Ph)CH(Ph)C}H_2$ *undergo oxidative coupling in the presence of copper salts to produce the corresponding neutral (μ-bis(carbene))dimanganese complexes* $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C(OEt)CH(R)CH(R)(OEt)C{=}\}$ *and* $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}\overline{CN(Ph)CH(Ph)C}HCHCH(Ph)N(Ph)C{=}\}$*. Double deprotonation of* $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C(OEt)CH_2CH_2(OEt)C{=}\}$ *gives a dianionic species that undergoes an intramolecular oxidative coupling in the presence of copper(II) to give the (μ-vinylbis(carbene))dimanganese complex (E)-*$\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C(OEt)CH{=}CH(OEt)C{=}\}$*. Controlled reduction of the latter gives a* Mn^0/Mn^I *mixed-valence complex which has been characterized by EPR.*

It is well established that hydrogen atoms α to the carbene carbon atom in "Fischer-type" carbene complexes are acidic[1] and can be easily removed upon treatment with bases to form carbene anions[2] or carbene "enolates", which possess in some aspects a chemistry similar to that of ketone or ester enolates.[3] This chemistry includes oxidative coupling induced by Cu(I) or Cu(II) salts.[4] Following investigations of the alkylalkoxycarbene complexes $Cp'(CO)_2Mn{=}C(OEt)CH_2R$,[5] we were interested in determining whether their deprotonated form would undergo oxidative coupling in the presence of copper salts to give bridging bis(carbene) complexes.[6,7]

The treatment of a solution of the carbene anion $[Li][Cp'(CO)_2Mn{=}C(OEt)CHR]$ ([**1a**]$^-$, R = H; [**1b**]$^-$, R = Me), generated in situ by reaction of $Cp'(CO)_2Mn{=}C(OEt)CH_2R$ (**1a**, R = H; **1b**, R = Me) with ^{n}BuLi in THF at −60 °C,[5a] with 0.6 molar equiv of Cu(I) iodide[8] followed by molecular oxygen yields the new (μ-bis(carbene))dimanganese complexes $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C(OEt)CH(R)CH(R)(OEt)C{=}\}$ (**2a**, R = H; **2b**, R = Me) (eq 1).[10,11] Complex **2b**, which bears two asymmetric carbon atoms, forms as an ~50:50 mixture of diastereoisomers. The use of a copper(II) salt, $CuCl_2$, as the oxidative coupling reagent is also effective in the reac-



(1)

⊗ Abstract published in *Advance ACS Abstracts*, November 15, 1994.

[1] (a) Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 390. (b) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230. (c) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1976**, *118*, 309. (d) Bernasconi, C. F.; Sun, W. T. *J. Am. Chem. Soc.* **1993**, *115*, 12526.

[2] Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1994**, *13*, 214.

[3] (a) Fischer, H.; Kreissel, F. R.; Schubert, U.; Hoffman, P.; Dötz, K. H.; Weiss, K. *Transition Metal Carbene Complexes*; VCH: Weinheim, Germany, 1983. (b) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5. (c) Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503. (d) Anderson, B. A.; Wulff, W. D.; Rahm, A. *J. Am. Chem. Soc.* **1993**, *115*, 4602. (e) Yi, C. S.; Geoffroy, G. L.; White, C. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 3806. (f) Wulff, W. D.; Anderson, B. A.; Toole, A. J.; Xu, Y.-C. *Inorg. Chim. Acta* **1994**, *220*, 215 and references therein.

[4] (a) Kauffmann, T.; Beissner, G.; Berg, H.; Köppelmann, J. L.; Schönfelder, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 540. (b) Rathke, M. W.; Lindert, A. *J. Am. Chem. Soc.* **1971**, *93*, 460. (c) Ito, Y.; Konoike, T.; Saegusa, T. *J. Am. Chem. Soc.* **1975**, *97*, 2912. (d) Ito, Y.; Konoike, T.; Harada, T.; Saegusa, T. *J. Am. Chem. Soc.* **1977**, *99*, 1487. (e) Kobayashi, Y.; Taguchi, T.; Morikawa, T. *Tetrahedron Lett.* **1978**, 3555. (f) Kobayashi, Y.; Taguchi, T.; Morikawa, T.; Tokuno, E.; Sekiguchi, S. *Chem. Pharm. Bull.* **1980**, *28*, 262.

[5] (a) Kelley, C.; Lugan, N.; Terry, M. R.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6735. (b) Terry, M. R.; Mercado, L. A.; Kelley, C.; Geoffroy, G. L.; Lugan, N.; Nombel, P.; Mathieu, R.; Haggerty, B. S.; Owens-Waltermire, B. E.; Rheingold, A. L. *Organometallics* **1994**, *13*, 843.

[6] (a) Macomber, D. W.; Hung, M.-H.; Madhukar, P.; Liang, M.; Rogers, R. D. *Organometallics* **1991**, 10, 737 and references therein. (b) Cron, S.; Morvan, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 1611. (c) Jordi, L.; Moretó, M.; Ricart, S.; Viñas, J. M.; Molins, E.; Miravitlles, C. *J. Organomet. Chem.* **1993**, *444*, C28.

[7] Lattuada *et al.* have briefly mentioned the formation of the (μ-bis(carbene))dichromium complex $\{(CO)_5Cr\}_2\{\mu\text{-}{=}C(OMe)CH_2CH_2(OMe)C{=}\}$ as a side product in the reaction of the anionic carbene $[Li][(CO)_5Cr{=}C(OMe)CH_2]$ with oxiranes preactivated by $TiCl_4$. The authors suggested that $TiCl_4$ could be responsible for the observed oxidative coupling: Lattuada, L.; Licandro, E.; Maiorana, S.; Molinari, H.; Papagni, A. *Organometallics* **1991**, *10*, 807.

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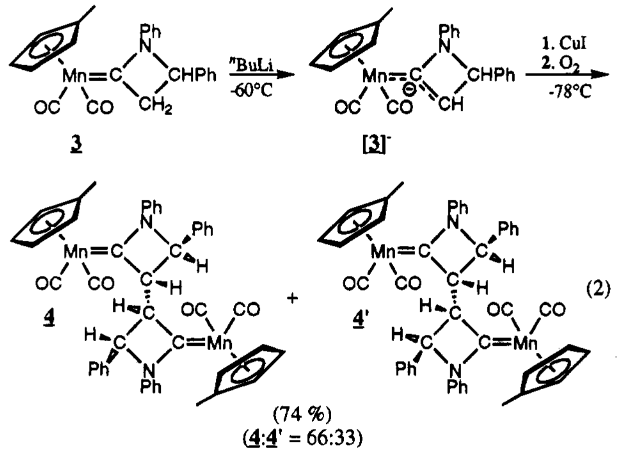
tion.[12] Finally, the oxidative coupling of the carbene anion [**1a**]$^-$ was also achieved by electro-oxidation.[13]

The overall reaction sequence shown in eq 1 can be viewed as a "dehydrodimerization"[14] reaction of *alkylalkoxycarbene* complexes. The reaction has been extended to the cyclic *aminocarbene* complex Cp′(CO)$_2$Mn=CN(Ph)C(H)PhCH$_2$ (**3**),[5b] which afforded the dehydrodimerization products **4** and **4′** in 74% overall yield (eq 2).



Considering the structure of **3**, a mixture of six different stereoisomers distinguishable by NMR could *a priori* form: two *meso* forms and four *dl* pairs. After the reaction, only two stereoisomers are observed, **4** and **4′**, in a 66:33 ratio.[10,15] They could be partially separated by fractional crystallization, and the structure of **4** has been determined by X-ray crystallography.[10,16] Compound **4** possesses a crystallographic inversion center, as seen in eq 2. Therefore, it is one of the two possible *meso* forms. The structure of the second stereoisomer **4′**, one of the *dl* pairs, has been deduced from the NMR data.

Saegusa *et al.* have shown that copper(II) salts promote the formation of olefinic diketones from 1,4-diketone dienolates.[4c] Considering this reaction, we anticipated that a similar treatment of the (μ-bis(carbene))dimanganese complexes **2** could lead to (μ-vinylbis(carbene))dimetal complexes. Indeed, the treatment of complex **2a** at low temperature with 2.2 molar equiv of ⁿBuLi followed by 2.2 molar equiv of copper(II) chloride gives the new (μ-vinylbis(carbene))dimanganese complex {Cp′(CO)$_2$Mn}$_2${μ-=C(OEt)CH=CH(OEt)C=} (**5**) in 36% yield.[10,17] The yield of **5** could be significantly improved by bubbling O$_2$ into the solution at low temperature after the addition of CuCl$_2$.[10,19] In that manner, complex **5** could be isolated in 62% yield (Scheme 1). Attempts to extend that reaction to complex **2b** failed, probably because hydrogen atoms α to the carbene atom are not acidic enough to be removed either by KH or ⁿBuLi.[19]

The structure of **5** has been determined by X-ray crystallography (Figure 1).[20] It has an *E* configuration around the C=C bond. The C(7)−C(8) bond is significantly longer than the C=C distance of an isolated double bond (1.299 Å)[21] and compares well with the C=C distance found in conjugated systems (1.330 Å),[21] illustrating a substantial delocalization of the double bond over the Mn(1)−C(5)−C(7)−C(8)−C(6)−Mn(2) chain.

It is likely that the formation of **5** from **2a** under the reaction conditions shown in Scheme 1 proceeds via the initial formation of a μ-bis(carbene) dianion resulting from a double deprotonation of **2a**, [Li]$_2$[**2a**], followed by an intramolecular oxidative coupling induced by the Cu(II) salt.[4c] Although we have not been able to directly observe that dianionic complex due to its thermal instability, its formation has been assayed by its reaction at low temperature with MeI, which afforded complex **2b** in nearly quantitative yield as a 60:40 mixture of diastereoisomers.[10]

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(8) Examination of the literature concerning the copper-salt-mediated oxidative coupling of ester or ketone enolates,[4] or more generally oxidative coupling of carbanions,[9] shows that 0.5 molar equiv of cuprous salt (usually followed by reaction with O$_2$), or 1 molar equiv of a cupric salt (sometimes followed by reaction with O$_2$), is usually required to obtain the best yields in coupling products.

(9) (a) Whitesides, G. M.; SanFilippo, J., Jr.; Casey, C. P.; Panek, E. J. *J. Am. Chem. Soc.* **1967**, *89*, 5302. (b) Jukes, A. E. *Adv. Organomet. Chem.* **1974**, *12*, 215. (c) Kauffman, Th. *Angew. Chem., Int. Ed. Engl.* **1974**, *5*, 291.

(10) The detailed experimental, spectroscopic, and crystallographic information are provided in the supplementary material.

(11) The carbene complex **1a** (1.9 mmol) was dissolved in 10 mL of THF, the solution was cooled to −60 °C, and ⁿBuLi (2.1 mmol) was added. After it was stirred for 30 min, the solution was cooled to −78 °C, and CuI (1.1 mmol) was added. When all of the solid CuI disappeared (~2 h), dry oxygen was bubbled into the solution for 30 s. The solvent was then removed under vacuum while the reaction flask was allowed to reach room temperature. The residue was extracted with ether and filtered on a short column of alumina. The filtrate was evaporated to dryness, and recrystallization of the residue from diethyl ether/hexane left complex **2a** as an orange microcrystalline compound in 63% yield. Selected data for **2a**: IR (ν(CO), THF) 1940, 1880 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 3.02 (s, 4H, −H_2CCH_2−); ^{13}C NMR (C$_6$D$_6$) δ 338.53 (Mn=*C*), 57.9 (−H$_2$*CC*H$_2$−). Anal. Calcd for C$_{24}$H$_{28}$Mn$_2$O$_6$: C, 55.17; H, 5.36. Found: C, 55.20; H, 5.44. Selected data for **2b** (mixture of diastereoisomers, **2b** and **2b′**): IR (ν(CO), THF) 1945, 1880 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 3.93 (AA′(X$_3$X′$_3$) pattern, 2H, $J_{AA'}$ = 6.7 Hz, J_{AX} = 6.9 Hz, −C*H*−) (**2b**)), 3.71 (AA′(X$_3$X′$_3$) pattern, 2H, $J_{AA'}$ = 10.7 Hz, J_{AX} = 6.5 Hz, −C*H*− (**2b′**)), 0.96 ((AA′)X$_3$X′$_3$ pattern, 3H, −CH(CH_3)− (**2b′**)), 0.91 ((AA′)X$_3$X′$_3$ pattern, 3H, −CH(CH_3)− (**2b**)); ^{13}C NMR (C$_6$D$_6$) δ 344.4 (Mn=*C*), 65.7, 65.5 (−*C*H(CH$_3$)*C*H(CH$_3$)− (**2b** and **2b′**)). Anal. Calcd for C$_{26}$H$_{32}$Mn$_2$O$_6$: C, 56.74; H, 5.86. Found: C, 56.27; H, 5.86.

(12) In the present instance, molecular oxygen is not required to achieve the coupling but its use significantly shortens the reaction time and improves the yield.[10]

(13) Cyclic voltammetry of a solution of the carbene anion [**1a**]$^-$ at −20 °C displayed an irreversible oxidation wave at 0.040 V (vs SCE) at a scan speed of 0.1 V/s. Bulk oxidation of [**1a**]$^-$ in THF/[ⁿBu$_4$N][PF$_6$] medium at 0.600 V (vs SCE) led to the formation of **2a**, which was isolated in 42% yield.

(14) Kauffman, T.; Kuhlmann, D.; Sahm, W.; Schreken, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 541.

(15) Selected data for **4**: IR (ν(CO), Et$_2$O) 1935, 1865 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 6.13 (s, 1H, −C*H*Ph), 3.75 (s, 1H, −C*H*−); ^{13}C NMR (C$_6$D$_6$) δ 296.1 (Mn=*C*(NPh)−), 78.7 (−*C*HPh−), 65.6 (−*C*H−). Selected data for **4′**: IR (ν(CO), Et$_2$O) 1935, 1865 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) 5.71 (s, 1H, −C*H*Ph), 3.95 (s, 1H, −C*H*−); ^{13}C NMR (C$_6$D$_6$) δ 295.5 (Mn=*C*(NPh)−), 75.7 (−*C*HPh−), 65.3 (−*C*H−). Anal. Calcd for C$_{46}$H$_{38}$Mn$_2$N$_2$O$_4$: C, 69.7; H, 4.83; N, 3.53. Found: C, 69.39; H, 5.29; N, 3.53.

(16) Crystal data for **4**: monoclinic, $C_{2h}{}^5$-$P2_1/n$, a = 10.039(2) Å, b = 8.523(1) Å, c = 22.821(2) Å, β = 94.56(1)°, V = 1946.5(5) Å^3, Z = 2, R = 0.060, R_w = 0.060 for 1806 observations and 184 variable parameters.[10]

(17) Selected data for **5**: IR (ν(CO), THF) 1940, 1885 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 6.85 (s, 2H, −*H*C=C*H*−); ^{13}C NMR (C$_6$D$_6$) δ 319.6 (Mn=*C*), 129.1 (s, −H*C*=*C*H−). Anal. Calcd for C$_{24}$H$_{26}$Mn$_2$O$_6$: C, 55.38; H, 5.00. Found: C, 55.27; H, 5.09.

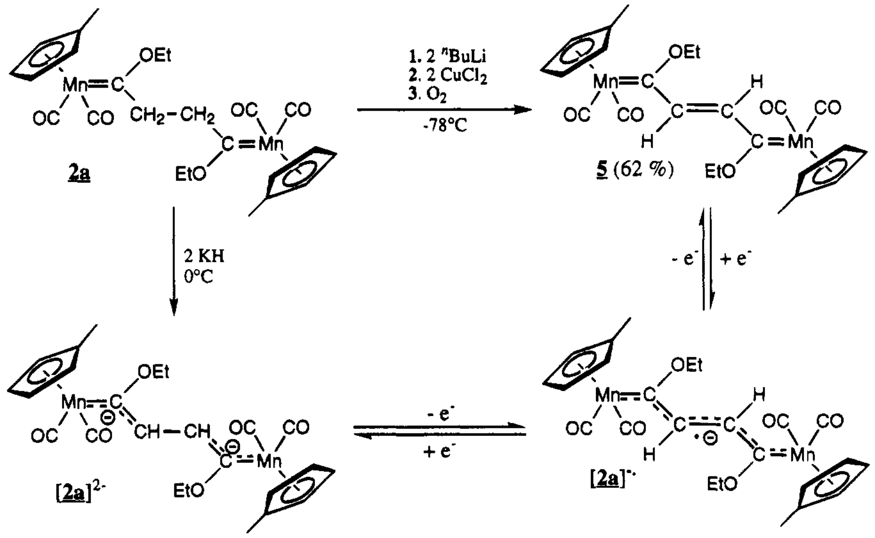
(18) At the present stage of our investigation, we do not fully understand the role of oxygen in that reaction. Note that, in the absence of Cu(II), oxygen alone readily decomposes [**2a**]$^{2-}$ to several unidentified compounds.

(19) (a) Although Casey *et al.* have reported that even a tertiary carbon atom attached to the carbene carbon atom in *chromium* Fischer-type carbene complexes can be deprotonated,[1c] the Cp′(CO)$_2$Mn fragment presents a poorer acceptor ability than the (CO)$_5$M (M = Cr, W) fragment[19b] and is less likely to stabilize tertiary carbanions that would form upon deprotonation of **2b**. (b) Dötz, K. H.; Böttcher, D.; Jendro, M. *Inorg. Chim. Acta* **1994**, *222*, 291.

(20) Crystal data for **5**: triclinic, $C_i{}^1$-$P\bar{1}$, a = 10.172(6) Å, b = 11.356(3) Å, c = 11.095(3) Å, α = 105.42(2)°, β = 93.07(5)°, γ = 108.06(5)°, V = 1162(1) Å^3, Z = 2, R = 0.032, R_w = 0.038 for 3407 observations and 289 variable parameters.[10]

(21) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

Scheme 1



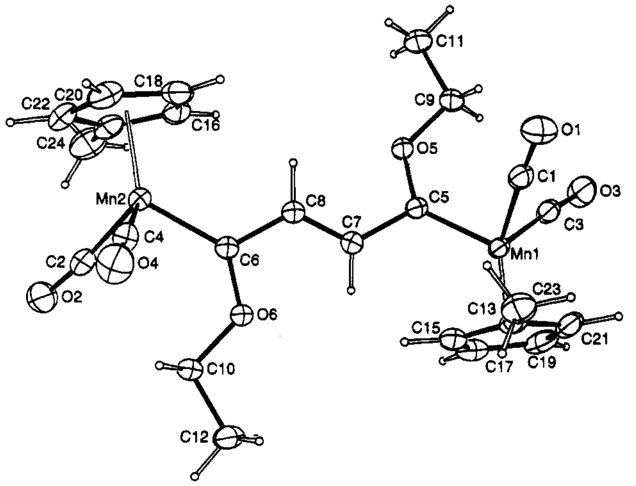


Figure 1. Perspective view of the complex (*E*)-{Cp′(CO)$_2$Mn}$_2${μ-=C(OEt)CH=CH(OEt)C=} (**5**). Selected bond distances and angles: Mn(1)–C(5) = 1.893(3) Å; C(5)–C(7) = 1.471(4) Å; C(7)–C(8) = 1.323(4) Å; Mn(2)–C(6) = 1.891(3) Å; C(6)–C(8) = 1.472(4) Å; C(5)–C(7)–C(8) = 124.2(2)°; C(6)–C(8)–C(7) = 124.9(2)°.

The dianion [K]$_2$[**2a**], generated by reaction of **2a** with 2.2 equiv of KH,[22] was found to be more stable. In comparison to **2a**, its IR spectrum displays two bands shifted by 75–100 cm^{-1} toward lower frequencies. The relative thermal stability of [K]$_2$[**2a**] allowed us to investigate its electrochemical behavior. Cyclic voltammetry (CV) of the complex [K]$_2$[**2a**] at 0 °C in THF/[^{n}Bu$_4$N][PF$_6$] medium (scan rate 0.1 V/s) displays two quasi-reversible one-electron-oxidation waves at −0.95 and −1.15 V (vs SCE). Under the same conditions, CV of **5** shows two quasi-reversible one-electron-reduction waves at the same potentials as for [**2a**]$^{2-}$. Both controlled reduction of **5** and controlled oxidation of [**2a**]$^{2-}$ on the plateau between the two oxidation–reduction waves leads to the formation of the same radical anion [**2a**]$^{\bullet-}$. The room-temperature EPR spectrum of this complex shows a hyperfine pattern that consists of an undecet of triplets ($g = 2.007$; $A_{\mathrm{Mn}} = 16.2$ G; $A_{\mathrm{H}} = 4.3$ G).[10] This pattern is consistent with a type III[23] Mn^0/Mn$^{\mathrm{I}}$ mixed-valence complex in which the unpaired electron is delocalized on the EPR time scale over the two manganese atoms. The electrochemical behavior of complexes [**2a**]$^{2-}$/**5** is reminiscent of that of closely related diiron or dirhenium complexes in which a C$_4$ unsaturated hydrocarbon chain spans the two metal centers.[24]

In summary, we have shown that carbene anions generated by deprotonation of alkoxy- or aminocarbene complexes of manganese bearing primary or secondary carbon atoms in the α position relative to the carbene carbon atom can undergo oxidative coupling in the presence of copper salts to give (μ-bis(carbene))dimanganese complexes in satisfactory yields. The oxidative coupling may also take place in an intramolecular fashion within a (μ-bis(carbene))dimanganese dianion to form a (μ-vinylbis(carbene))dimanganese complex. Further investigations of the reactivity of the unusual (μ-bis(carbene))dimanganese dianion and in the direction of (μ-bis(carbyne))dimanganese complexes are in progress.

Acknowledgment. We gratefully acknowledge NATO for a travel grant to N.L. and G.L.G. Thanks are due to Dr. D. de Montauzon for the electrochemical studies and to Dr. A. Mari for recording the EPR spectra and for helpful discussions.

Supplementary Material Available: Text giving experimental and spectroscopic data for all the new complexes, full experimental data for the X-ray studies and tables of atomic coordinates, anisotropic temperature factors, and bond distances and angles for **4** and **5**, and figures showing a perspective view of **4** and both experimental and simulated EPR spectra of [**2a**]$^{\bullet-}$ (13 pages). Ordering information is given on any current masthead page.

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[22] THF (10 mL) was added at 0 °C to a solid mixture of **2a** (0.150 g, 0.29 mmol) and KH (0.027 g, 0.69 mmol). The reaction was monitored by IR until the bands due to **2a** totally disappeared (~2 h) and substituted by those of [K]$_2$[**2a**]. [K]$_2$[**2a**]: IR (ν(CO), THF) 1865, 1780 cm^{-1}. As far as the intramolecular coupling reaction is concerned, the reactivity of [K]$_2$[**2a**] is the same as that of [Li]$_2$[**2a**]. Nevertheless, from a practical point of view, it is better to use ^{n}BuLi to deprotonate **2a**.

[23] Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247

[24] (a) Seyler, J. W.; Weng, W.; Zhou, Y.; Gladysz, J. A. *Organometallics* **1993**, *12*, 3802. (b) Le Narvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 357. (c) Etzenhouser, B. A.; DiBiase Cavanaugh, M.; Spurgeon, H. N.; Sponsler, M. B. *J. Am. Chem. Soc.* **1994**, *116*, 2221.