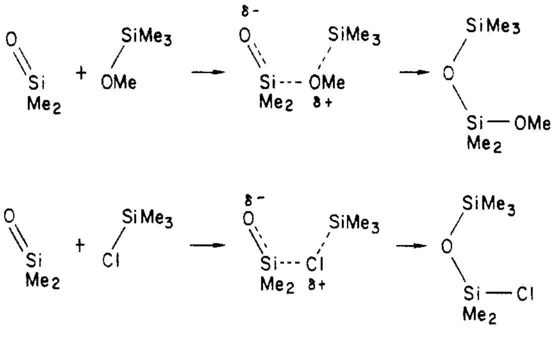
Scheme II



at silicon.[13] Although a silyl shift from oxygen to carbon would be endothermic, it can occur if there is some suitable driving force, such as the concomitant formation of a carbon–oxygen π-bond at the expense of a weaker carbon–carbon π-bond.[13] In Scheme I, the necessary driving force would be provided by the initial addition, forming a "hot" intermediate that is chemically activated for the 1,3-shift.

(v) A similar stepwise mechanism would then account for the reaction of 2 with methoxytrimethylsilane and with trimethylchlorosilane, involving 1,3-silyl shifts from oxygen to oxygen and from chlorine to oxygen, respectively. As the "hot" intermediate formed initially would be "hotter" than in Scheme I because of the enhanced reactivity of 2 toward nucleophiles,[9] a wider range of silyl shifts would be expected than are observed in unactivated molecules.[13] While it is conceptually convenient to envisage these reactions as occurring in two distinct stages, there is probably no intermediate minimum along the reaction coordinate (cf. the dimerization of silanone[9]).

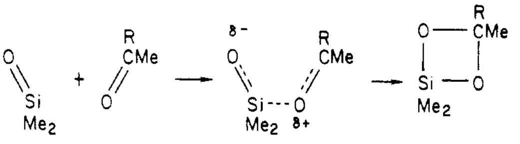
A further indicator of mechanistic dichotomy is provided by the measured *A* factor differences; reactions 2 and 3 have about the same *A* factor, while the *A* factor for reaction 1, which presumably does occur via a tight four-center transition state, is almost two powers of 10 lower. These reactions are illustrated in Scheme II.

(vi) Of the reactions in Schemes I and II, reaction 3 requires the highest activation energy, probably because Cl is a poorer nucleophile than O and does not form a positive, two-coordinate intermediate as readily. These factors could account for the failure of 3 to react with trimethylchlorosilane.

(vii) According to the foregoing ideas, neither 2 nor 3 would be expected to react readily with Et_2O, CH_2Cl_2, or Me_3SiH because these molecules are too bulky for the four-center reaction and do not have labile groups which would undergo 1,3-shifts in the stepwise mechanism.

(viii) We can only speculate as to the structure of the 1:1 adducts of 2 with acetone and acetaldehyde because our evidence is based solely on mass spectra. The adducts were observed to decompose at 440 °C, accounting for earlier failures to observe them with sources of 2 that required higher temperatures. If they are cyclic adducts, they could have been formed by addition followed by ring closure, as in Scheme III.

Scheme III



In our earlier comments[4] on the mechanism of formation of D_3 from 2 we showed that D_3 formation could not result from self-reaction of 2, forming successively "D_2" and then D_3, if the rate constant for dimerization of 2 was similar to that[11] for dimerization of 3. As noted in (i) above, it now seems that 3 is sufficiently less polar than 2 to undergo cycloadditions more readily than 2; if so, self-reaction of 2 to form "D_2" then D_3 may occur by head-to-tail addition with a rate constant sufficiently higher than that for the cyclodimerization of 3 for self-reaction of 2 to be a feasible route to D_3 [see comment on *A* factors in (v) above]. Nevertheless, we continue to think it more likely that D_3 is mainly formed in a cycle of reactions involving a molecular species with which 2 reacts rapidly, either homogeneously or heterogeneously, such as water.[4]

Acknowledgment. We thank the SERC and Dow Corning (Europe) Ltd. for support. We also thank Elsa Brackenbury and Richard Pocock for some of the kinetic measurements, undertaken during their undergraduate project work.

Registry No. 1, 65181-02-4; 2, 47956-45-6; 3, 61153-00-2.

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Reactions at the β-Carbon of Anionic Tungsten Acetylide Complexes: Ion Pairing, Vinylidene Formation, and CO_2 Binding

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Received July 16, 1985

Summary: Addition of CO_2 to the β-carbon of Li[*fac*-$(OC)_3$(dppe)WC≡CR] (R = Me, *n*-Bu) followed by methylation yields vinylidene products, *mer*-$(OC)_3$(dppe)W=C=C(R)CO_2Me. Ion-pair formation at the β-carbon may act as a kinetic mediator in this system. We also report syntheses of *mer*-$(OC)_3$(dppe)W=C=CRR′ complexes, including the parent C=CH_2 derivative.

Coordination of acetylide anions to tungsten(0) effectively transfers the nucleophilicity of the C_2 fragment from C_α to C_β. Anionic complexes 1–4 (Scheme I) were prepared as alkali-metal salts by addition of the appropriate acetylide reagent to a THF solution of (acetone).[1] Table I contains ν_{CO} and $\nu_{C\equiv C}$ infrared data for the lithium, sodium, and PPN salts of [*fac*-$(OC)_3$(dppe)WC≡CR]$^-$ (R = H, 1; Me, 2). Changing the cation from PPN^+ to Na^+ to Li^+ results in an increase in the carbonyl CO frequencies. The simultaneous decrease observed for $\nu_{C\equiv C}$ in 2 is evidence of site selective ion pairing between the β-carbon and the alkali cations (Scheme I). This site selectivity is

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(1) Yellow M[*fac*-$(OC)_3$(dppe)WC≡CR] salts (M = Li, Na; dppe = $Ph_2PCH_2CH_2PPh_2$) were isolated in good yields (60–95%). PPN salts (PPN = bis(triphenylphosphine)nitrogen(1+)) were prepared by ion exchange in CH_2Cl_2. IR data for 1–4 are presented in Table I. See ref 18 for preparation of $(OC)_3$(dppe)W(acetone). [PPN][*fac*-$(OC)_3$(dppe)-WC≡CH], 1: ^{1}H NMR (CD_2Cl_2) δ 7.97–7.10 (m, Ph), 2.75 (m, PC*H*HC*H*HP), 2.45 (m, PCH*H*CH*H*P), 1.39 (t, $^4J_{HP}$ = 3.5 Hz, W–CC*H*); ^{13}C NMR (^{1}H coupled, CD_2Cl_2) δ 201.9 (m, CO), 200.2 (m, CO) 140.0–126.4 (m, Ph), 99.5 (d, $^1J_{CH}$ = 213 Hz, W–C*C*H), 28.6 (tm, $^1J_{CH}$ = 126 Hz, P*C*H$_2$*C*H$_2$P), (α-carbon of acetylide not observed).

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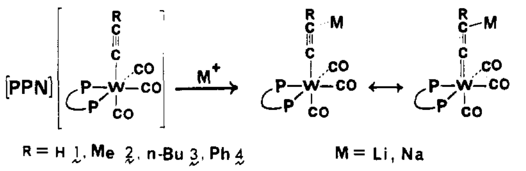
Scheme I



Scheme II

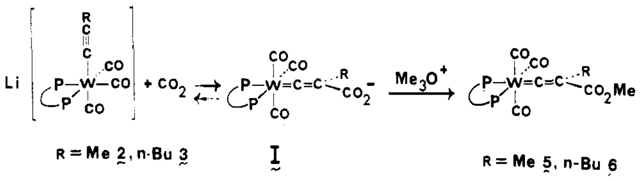


Table I. Infrared Data for $[fac\text{-}(OC)_3(dppe)WC\equiv CR]^-$

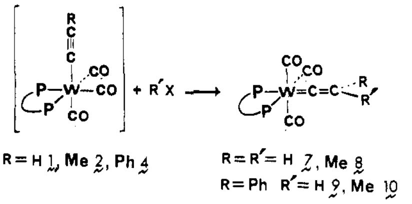
complex	ν_{CO}[a]	$\nu_{C\equiv C}$
Li[*fac*-$(OC)_3$(dppe)W(C≡CH)]	1892 s, 1806 s	1927 m
Na[*fac*-$(OC)_3$(dppe)W(C≡CH)]	1892 s, 1803 s	1927 m
PPN[*fac*-$(OC)_3$(dppe)W(C≡CH)][b]	1887 s, 1795 s, 1768 s	1922 m
Li/HMPA[*fac*-$(OC)_3$(dppe)W(C≡CH)][b,c]	1886 s, 1799 s, 1767 s	1920 m
Li[*fac*-$(OC)_3$(dppe)W(C≡CMe)]	1905 s, 1805 s	2058 vw
Na[*fac*-$(OC)_3$(dppe)W(C≡CMe)]	1898 s, 1795 s	2065 vw
PPN[*fac*-$(OC)_3$(dppe)W(C≡CMe)]	1896 s, 1801 s, 1772 s	2075 vw
Li[*fac*-$(OC)_3$(dppe)W(C≡C(*n*-Bu))]	1905 s, 1801 s	2055 vw
Li[*fac*-$(OC)_3$(dppe)W(C≡CPh)]	1910 s, 1805 s	2030 w

[a] All frequencies are reported as cm^{-1}. Spectra were recorded in THF solution unless otherwise specified. [b] Recorded in CH_2Cl_2 solution. [c] Prepared by addition of 1 equiv of hexamethylphosphoramide (HMPA) to the lithium salt of 1 in CH_2Cl_2.

in accord with the known reactivity of transition-metal acetylide complexes;[2] molecular orbital calculations on $(\pi\text{-}C_5H_5)Fe(CO)_2(C\equiv CR)$ indicate that the HOMO is localized on the acetylide β-carbon.[3] Similar infrared changes have been reported for other tight ion pairs involving anionic metal carbonyl complexes with ligands other than CO acting as nucleophiles[4] (e.g., in $Na[Fe(CO)_4CN]$ ion pairing lowers $\nu_{C\equiv N}$ while the CO frequencies increase[5]).

Lithium salts of 2 and 3 react with CO_2 between −78 and 0 °C to produce a meridional intermediate (I), assumed to be the carboxylate derivative formed by addition of CO_2 to C_β. Methylation with $[Me_3O][BF_4]$ and chromatographic workup yield carbomethoxyvinylidene complexes *mer*-$(OC)_3$(dppe)W=C=CR(CO_2Me) (R = Me, 5; R = *n*-Bu, 6, Scheme II).[6] The vinylidene ligand in 6 was identified by ^{13}C NMR: δ 333.7 (dd, $^2J_{CP}$ = 17, 7 Hz, C_α), 119.8 (d, ($^3J_{CP}$ = 10 Hz, C_β).[7] The ^{13}C NMR parameters are close to those of *mer*-$(OC)_3$(dppe)W=C=CH(CO_2Me).[8] The lithium salt of the phenyl acetylide derivative 4 does not react with CO_2 over a 24-h period. Attempts to make dithiocarbomethoxy analogues of 5 and 6 by addition of CS_2 to the acetylide reagents resulted in intractable mixtures.[9]

Scheme III



The PPN salt of 2 does not react with CO_2 over a period of 24 h. Sodium salts of 1 and 2 react rapidly to generate analogues of intermediate I, but addition of alkylating reagents leads to decomposition rather than formation of carbomethoxyvinylidene products. Large counterion effects have been observed previously in reactions of transition-metal complexes with carbon dioxide.[10] It has been suggested that alkali cations interact with CO_2 oxygens in the transition state for CO_2 insertion into the metal–alkyl bond of $[W(CO)_5Me]^-$ and also form a tight ion pair with the carboxylate product.[11] The low-frequency ν_{CO} of the carboxylate group in intermediate I (1669 cm^{-1}) suggests a similar interaction here.

Fluoroboric acid reacts immediately with a THF slurry of the *fac*-acetylide complex 4 while methyl iodide reacts more slowly with 2 or 4 to form *mer*-vinylidene complexes (Scheme III). We believe the unsubstituted vinylidene 7, synthesized from HBF_4 and the sodium salt of 1 in CH_2Cl_2, is the first group 6 parent vinylidene to be isolated[12] (R = R′ = H, 7; R = R′ = Me, 8; R = H, R′ = Ph,

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(2) (a) Bruce, M. I.; Wallis, R. C. *J. Organomet. Chem.* **1978**, *161*, C1. (b) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763. (c) Wong, A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4948. (d) Wolf, J.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 414. (e) Berke, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 86. (f) Mayr, A.; Schaefer, K. C.; Huang, E. Y. *J. Am. Chem. Soc.* **1984**, *106*, 1517.

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(5) Darensbourg, M. Y.; Barros, H. L. C. *Inorg. Chem.* **1979**, *18*, 3286.

(6) Preparation of Complex 5: To *fac*-$(OC)_3$(dppe)W(acetone) (0.79 g, 1.09 mmol) in 40 mL of THF was added Li(CCMe) (0.10 g, 2.11 mmol) yielding a yellow solution in 5 min. When the reaction was judged complete by IR, the mixture was cooled to −78 °C and dry CO_2 was bubbled into the solution for 4 min. The sealed reaction flask was slowly warmed to 0 °C (the CO_2 pressure was periodically released). IR showed a meridional CO pattern (2010 m, 1920 s, 1899 vs cm^{-1}) at 0 °C. To this mixture at 0 °C was added $[Me_3O][BF_4]$ (0.30 g, 2.02 mmol). The reaction was stirred at 0 °C for 5 min and stirred at room temperature for another 15 min. The solvent was removed and the residue was purified by chromatography on Florisil eluting an orange band with a 1:1 ether/THF mixture. An orange powder was obtained in 63% yield. Orange crystals are obtained from CH_2Cl_2/hexanes: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 2010 m, 1945 m, 1908 s, ν_{COO} 1663 m; ^1H NMR ($CDCl_3$) δ 7.78–7.25 (m, Ph), 3.37 (s, OMe), 2.65 (m, PCH_2CH_2P), 1.92 (s, Me).

Complex 6 was prepared analogously to 5: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 2010 m, 1945 m, 1908 s; ν_{COO} 1655 m; ^1H NMR ($CDCl_3$) δ 7.86–6.92 (m, Ph), 3.32 (s, OMe), 2.66 (m, PCH_2CH_2P), 2.28 (t, $^3J_{HH}$ = 7 Hz, $C{=}C(R)(CH_2Pr)$), 1.63–1.18 (m, $C{=}C(R)CH_2CH_2CH_2Me$), 0.88 (t, $^3J_{HH}$ = 8 Hz, $C{=}C(R)(CH_2)_3CH_3$); ^{13}C ^1H-decoupled NMR ($CDCl_3$) δ 333.7 (dd, $^2J_{CP}$ = 17, 7 Hz, M=*C*=CRR′), 209.5 (br d, $^2J_{CP}$ = 14 Hz, CO trans to P), 202.2 (br s, 2 trans CO's), 169.5 (s, –*C*(O)OMe), 136.5–128.4 (m, Ph), 119.8 (d, $^2J_{CP}$ = 10 Hz, M=C=*C*RR′), 49.8 (s, OMe), 32.9 (s, $C{=}C(R)CH_2Pr$), 29.9 (m, PCH_2CH_2P), 28.7 (m, PCH_2CH_2P), 25.6 (s, $C{=}C(R)CH_2CH_2Et$), 22.6 (s, $C{=}C(R)(CH_2)_2CH_2Me$), 14.1 (s, $C{=}C(R)(CH_2)_3Me$).

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(8) Birdwhistell, K. R.; Burgmayer, S. J. N.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 7789.

(9) See: Selegue, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 119 for formation of dithiocarbomethoxyvinylidene products from iron reagents and CS_2.

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9; R = Me, R′ = Ph, **10**).[13]

Proton NMR spectra of **7** and **8** display only one signal for the two vinylidene substituents at −95 °C (a doublet of doublets for **7** at 3.48 ppm with $^4J_{HP}$ = 4.5 and 3.0 Hz; a singlet for the methyl protons of **8** at 2.04 ppm). The structure of *mer*-$(OC)_3$(dppe)W=C=C(H)CO_2Me,[8] with the vinylidene ligand nearly in the WP_2 plane, has the two vinylidene substituents in different environments. The ^{1}H NMR data and the expected ground-state vinylidene orientation indicate that vinylidene rotation is rapid on the NMR time scale, in accord with a calculated barrier of only 5.9 kcal/mol for the model compound *mer*-$(OC)_3(H_2PCH_2CH_2PH_2)W{=}C{=}CH_2$.[14] The orientational preference of the vinylidene ligand is small in **7** and **8** because the dominant π-acceptor orbital of the α-carbon finds a filled dπ orbital of similar energy and extension in all orientations. Vinylidene[15] and allenylidene[16] ligands rotate rapidly in other systems.

To probe whether the facial to meridional rearrangement accompanying conversion of the acetylide reagent **4** to the vinylidene product **9** involved CO loss, a solution of **4** in THF was protonated under 1 atm of ^{13}CO. The absence of ^{13}CO in the vinylidene product **9** suggests that the isomerization is intramolecular. Facile intramolecular rearrangements of six-coordinate carbonyl derivatives are well documented;[17] the facial to meridional isomerization of $M(CO)_3(dppe)(\eta^2\text{-olefin})$(M=Mo, W) complexes is particularly relevant.[18]

Acknowledgment. We thank the National Science Foundation (CHE8310121) and donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. **1**·Li, 98586-58-4; **1**·Na, 98586-59-5; **1**·PPN, 98586-61-9; **1**·Li/HMPA, 98586-62-0; **2**·Li, 98586-63-1; **2**·Na, 98586-64-2; **2**·PPN, 98586-66-4; **3**·Li, 98586-67-5; **4**·Li, 98586-68-6; **5**, 98586-71-1; **6**, 98611-58-6; **7**, 98586-72-2; **8**, 98586-73-3; **9**, 88035-90-9; **10**, 96454-56-7; I (R = Me), 98586-69-7; I (R = *n*-Bu), 98586-70-0; *fac*-$(OC)_3$(dppe)W(acetone), 84411-66-5; *mer*-$(OC)_3(H_2PCH_2CH_2PH_2)W{=}C{=}CH_2$, 98586-74-4; LiCCH, 1111-64-4; LiCCMe, 4529-04-8; LiCCBu, 17689-03-1; LiCCPh, 4440-01-1; NaCCH, 1066-26-8; NaCCMe, 10486-71-2; CO_2, 124-38-9.

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[12] (a) Rudler proposed $(OC)_5W{=}C{=}CH_2$ as an intermediate. Levisalles, J.; Rudler, H.; Jeannin, Y.; Dahan, F. *J. Organomet. Chem.* **1979**, *178*, C8. (b) For other terminal unsubstituted vinylidenes, see ref 2b,c. (c) Werner H.; Wolf, J.; Zolk, R.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 981. (d) For bridging unsubstituted vinylidenes see Werner, H.; Wolf, J.; Muller, G.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 431. (e) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911. (f) Al-Obaidi, Y. N.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319. (g) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499. (h) Folting, K.; Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3483.

[13] Complex **7**: Addition of 0.1 mL of 0.1 M HBF_4(aq) to a yellow slurry of Na[*fac*-$(OC)_3$dppeW(CCH)] (0.33 g, 0.46 mmol) at 0 °C resulted in an immediate red color. The mixture was kept at 0 °C and dried over $MgSO_4$. The mixture was filtered, and the filtrate was reduced to 5 mL. Addition of hexanes precipitated **7** as a green powder in 53% yield: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 2000 m, 1925 s, 1883 vs, $\nu_{C=C}$ 1593 m; ^{1}H NMR (CD_2Cl_2) δ 7.91–6.84 (m, Ph), 3.48 (dd, $^4J_{HP}$ = 4.5, 3 Hz), 2.72 (m, PCH_2CH_2P); ^{13}C NMR (CD_2Cl_2) δ 332.7 (m, $W{=}\mathit{C}{=}CH_2$), 212.9 (m, CO trans to P), 203.9 (m, 2 trans CO's), 136.1–126.3 (m, Ph), 97.2 (td, $^1J_{CH}$ = 157 Hz, $^3J_{CP}$ = 14 Hz, $W{=}C{=}\mathit{C}H_2$), 30.5 (m, $P\mathit{C}H_2CH_2P$), 28.0 (m, $PCH_2\mathit{C}H_2P$). **8**: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1978 w, 1918 m, 1878 vs, $\nu_{C=C}$ 1667 w. **9**: IR (KBr, cm^{-1}) ν_{CO} 2000 m, 1895 s, 1875 vs, $\nu_{C=C}$ 1612 m, 1578 m. **10** has been previously reported, see: Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474.

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A Reversible Metal Framework Rearrangement Assisted by Coordinated Iodide. X-ray Structure Analysis of $[(Ph_3P)_2N][H_2Os_4(CO)_{12}(I)]$

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Summary: The complex $[(PPh_3)_2N]^+[H_2Os_4(CO)_{12}(I)]^-$, obtained by deprotonation of the butterfly cluster $H_3Os_4(CO)_{12}(\mu\text{-I})$ with $[(PPh_3)_2N][NO_2]$, is shown by X-ray analysis to consist of a tetrahedral arrangement of metal atoms with the two hydrides bridging adjacent edges and a terminally bonded iodide ligand. Protonation of the anion regenerates the parent neutral complex in a novel reversible structural transformation assisted by the iodide ligand. Crystal data: monoclinic, space group $P2_1/a$, a = 16.841 (2) Å, b = 20.699 (1) Å, c = 29.249 (3) Å, β = 90.91 (2)°, V = 10194.7 Å^3, and Z = 8.

The catalytic potential of coordinatively saturated metal clusters is conditioned by the formation of a vacant coordination site at some stage in the cycle. In the catalytic hydrogenation of ethylene with $HOs_3(CO)_{10}(OSi{\equiv})$, for instance, the formation of the required vacant site has been proposed to involve the reversible opening of the Os–O–Os bridge.[2] Therefore, the presence of ligands with such ability to modify their bonding mode could result in an enhanced reactivity of metal clusters.

Halide ligands on metal clusters can be bound either as doubly bridging, 3e donors, or terminal, 1e donors.[3] Thus,

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