Communications

Trigonal-Bipyramidal and Square-Pyramidal Tungstacyclobutane Intermediates Are Both Present in Systems in Which Olefins Are Metathesized by Complexes of the Type W(CHR′)(N-2,6-C_6H_3-*i*-Pr_2)$(OR)_2$

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Summary: Neopentylidene complexes of the type W(CH-*t*-Bu)(NAr)$(OR)_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2; OR = O-*t*-Bu, $OCMe_2(CF_3)$, OAr) react with ethylene to give trigonal-bipyramidal or square-pyramidal tungstacyclobutane complexes. A square-pyramidal form is observed when OR = O-*t*-Bu. Both forms are present when OR = $OCMe_2(CF_3)$ or OAr, and they interconvert at a rate that is on the order of the NMR time scale. Unsubstituted metallacycles react with excess neohexene to give square-pyramidal W[CH_2CH(*t*-Bu)CH_2](NAr)$(OR)_2$ complexes (OR = O-*t*-Bu, $OCMe_2(CF_3)$, OAr). W[CH_2CH(*t*-Bu)CH_2](NAr)[$OCMe_2(CF_3)$]$_2$ has been characterized crystallographically (space group $P4_2/n$, a = 25.26 (2) Å, c = 9.720 (5) Å, V = 6202 Å^3, M_r = 711.48, ρ(calcd) = 1.524 g cm^{-3}, Z = 8, μ = 40.05 cm^{-1}, R = 0.056, R_w = 0.082). The reaction between W[CH_2CH(*t*-Bu)CH_2](NAr)$(OAr)_2$ and ethylene to give W[$CH_2CH_2CH_2$](NAr)$(OAr)_2$ and *tert*-butylethylene is zero-order in ethylene and first-order in tungsten between 9 and 34 °C with $\Delta H^{\ddagger}$ = 19.8 (4) kcal mol^{-1}, $\Delta S^{\ddagger}$ = −6 (1) eu, and $\Delta G^{\ddagger}_{298}$ = 21.6 (7) kcal mol^{-1}.

The activity of olefin metathesis catalysts of the type W(CHR′)(NAr)$(OR)_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2; R′ = alkyl; R = alkyl, fluoroalkyl, or aryl)[1] depends dramatically upon the nature of OR, e.g., from ~10^3 turnovers min^{-1} when OR = $OCMe(CF_3)_2$ to virtually none when OR = O-*t*-Bu.[2] Tungstacyclobutane complexes W[CH(TMS)CH(TMS)CH_2](NAr)[$OCMe(CF_3)_2$]$_2$ and W($CH_2CH_2CH_2$)(NAr)[$OC(CF_3)_2(CF_2CF_2CF_3)$]$_2$ have been characterized through X-ray studies[1] and found to be approximately trigonal bipyramids with the WC_3 ring in the equatorial plane.[3] We now find that square-pyramidal tungstacyclobutane complexes are also present in these systems.

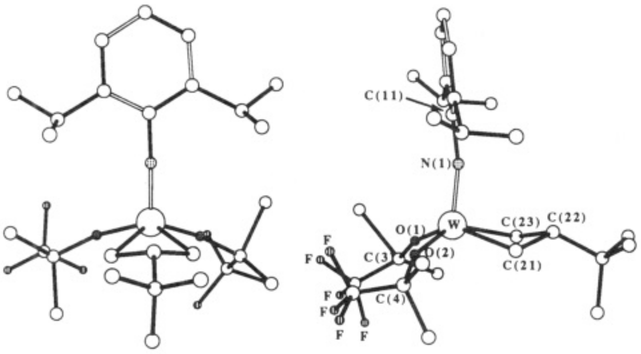


Figure 1. Molecular structure of W[CH_2CH(*t*-Bu)CH_2](NAr)[$OCMe_2(CF_3)$]$_2$ (**1d**). Selected bond lengths (Å) and angles (deg): W–O(1) = 1.869 (7), W–O(2) = 1.886 (6), W–N(1) = 1.736 (7), O(1)–W–O(2) = 99.6 (3), O(2)–W–C(21) = 87.4 (3), O(1)–W–C(23) = 89.2 (3), N(1)–W–O(1) = 113.9 (3), N(1)–W–O(2) = 111.7 (3), N(1)–W–C(23) = 98.4 (3), N(1)–W–C(2) = 99.4 (4), W–O(1)–C(3) = 164.4 (7), W–O(2)–C(4) = 158.6 (7), W–N(1)–C(11) = 167.9 (7) (see also Figure 2).

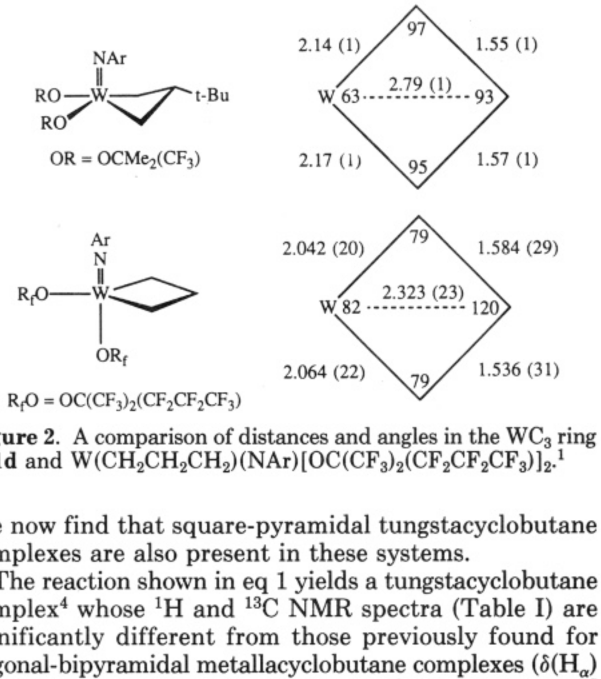
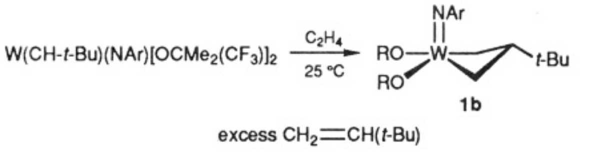


Figure 2. A comparison of distances and angles in the WC_3 ring in **1d** and W($CH_2CH_2CH_2$)(NAr)[$OC(CF_3)_2(CF_2CF_2CF_3)$]$_2$.[1]

The reaction shown in eq 1 yields a tungstacyclobutane complex[4] whose ^{1}H and ^{13}C NMR spectra (Table I) are significantly different from those previously found for trigonal-bipyramidal metallacyclobutane complexes ($\delta(H_\alpha) \approx 5$, $\delta(H_\beta) \approx -1$; $\delta(C_\alpha) \approx 100$, $\delta(C_\beta) \approx 0$).[1] An X-ray study[5]



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[1] Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.

[2] (a) Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 1169. (b) The rate also depends dramatically on the size of R′. The most recent studies[2c] suggest that W(CHEt)(NAr)(O-*t*-Bu)$_2$ reacts with ordinary internal olefins (e.g., *cis*-2-pentene) at a rate on the order of ~2 h^{-1}. (c) Yap, K.; Schrock, R. R., unpublished results.

[3] The bond lengths and angles in the WC_3 rings of the two compounds are essentially the same, even though the ring in W[CH(TMS)CH(TMS)CH_2](NAr)[$OCMe(CF_3)_2$]$_2$ is bent and that in W($CH_2CH_2CH_2$)(NAr)[$OC(CF_3)_2(CF_2CF_2CF_3)$]$_2$ is planar.

[4] Ethylene (1.1 mmol) was added via vacuum transfer to a solution of 150 mg (0.219 mmol) of W(CH-*t*-Bu)(NAr)[$OCMe_2(CF_3)$]$_2$[1] and 424 μL (3.29 mmol) of *tert*-butylethylene in 3.0 mL of pentane. After the solution had been stirred at 25 °C for 30 min, it was concentrated to a volume of ~0.25 mL and cooled to −40 °C. **1b** (108 mg, 0.152 mmol, 69%) was isolated as a yellow, microcrystalline solid after the mother liquor was removed by pipette. Calcd for $WC_{27}H_{46}F_6NO_2$: C, 45.58; H, 6.09. Found: C, 45.86; H, 6.14.

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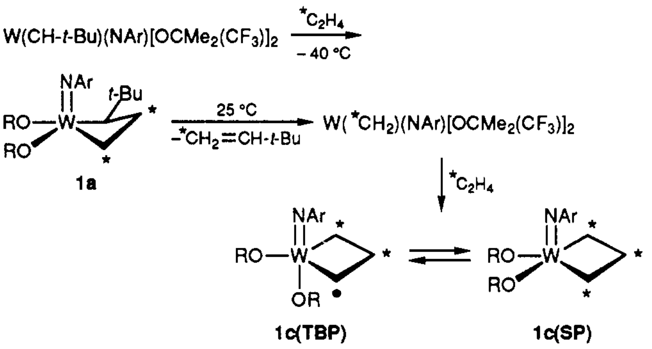
Table I. ^{1}H and ^{13}C NMR Data for Square-Pyramidal Tungstacyclobutane Complexes[a]

compound	$\delta(H_\alpha)$[b]	$\delta(H_\beta)$	$\delta(C_\alpha)$ (J_{CH})	$\delta(C_\beta)$ (J_{CH})	$J_{C_\alpha C_\beta}$
$W[CH(t\text{-}Bu)CH_2CH_2](NAr)[OCMe_2(CF_3)]_2$ (**1a**)	2.28 1.80	4.11 2.60	48.2 (127)[c]	24.1 (128)	32
$W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ (**1b**)[d]	2.36 1.12	2.62	47.1 (126)	46.0 (127)	
$W(CH_2CH_2CH_2)(NAr)[OCMe_2(CF_3)]_2$ (**1c**)	2.29	4.30 2.78	43.6 (134)	24.2 (134)	28
$W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ (**2b**)[d]	2.39 1.2[e]	2.71	48.5 (133)	45.1 (133)	
$W(CH_2CH_2CH_2)(NAr)(OAr)_2$ (**2c**)	2.35 3.02	4.43	43.5 (138)	22.6 (133)	29
$W[CH(t\text{-}Bu)CH_2CH_2](NAr)(O\text{-}t\text{-}Bu)_2$ (**3a**)	2.35 1.52	4.30 2.72	45.4 (131)[c]	24.9 (132)	33
$W[CH_2CH(t\text{-}Bu)CH_2](NAr)(O\text{-}t\text{-}Bu)_2$ (**3b**)[d]	2.36 1.10	2.68	44.9 (130)	46.8 (125)	
$W(CH_2CH_2CH_2)(NAr)(O\text{-}t\text{-}Bu)_2$ (**3c**)	2.3	4.4 2.8	41.9	24.5	30

[a] In toluene-d_8 unless otherwise noted. Coupling constants in Hz. [b] In some instances not all the α-proton resonances were located due to interference by other signals. [c] Only the CH_2 C_α resonance is reported. [d] Spectrum recorded in C_6D_6. [e] Approximate chemical shift according to a COSY spectrum.

Scheme I

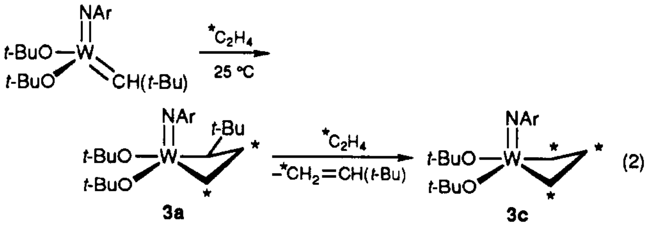


revealed that the product **1b** is a square-pyramidal tungstacyclobutane complex (Figure 1) in which the imido ligand occupies the apical position. Comparison (Figure 2) of the bent ring in **1b** (dihedral angle 33.4°) with the planar ring in structurally characterized trigonal-bipyramidal $W(CH_2CH_2CH_2)(NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$ reveals differences that are consistent with the rather different core geometries. Potentially important differences are the smaller C_α–W–C_α angle in **1b** (63° vs. 82°), the consequently much longer W$\cdots$$C_\beta$ distance (2.79 (1) Å vs 2.323 (23) Å) and the longer W$\cdots$$C_\alpha$ distance ($\sim$2.15 vs $\sim$2.05 Å).

The reaction between $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2(CF_3)]_2$ and excess $^{13}C_2H_4$ at -40 °C in toluene-d_8 proceeds readily to give a single species (**1a**) quantitatively that is characterized by ^{13}C NMR resonances at 48.2 (d) and 24.1 (d) ppm (J_{CC} = 32 Hz; Scheme I, *C = ^{13}C; Table I).[6] After the sample was warmed to room temperature and cooled back to -40 °C, resonances are observed for $\sim$1 equiv of $^{13}CH_2{=}CH\text{-}t\text{-}Bu$ and *two* unsubstituted tungstacycles. The resonances at 98.8 (d) and 3.59 (t) ppm (J_{CC} = 13 Hz) can be ascribed to the α- and β-carbon atoms of a trigonal-bipyramidal unsubstituted tungstacyclobutane complex (**1c(TBP)**) analogous to those observed previously,[1] while the resonances at 43.6 (d) and 24.2 (t) ppm (J_{CC} = 28 Hz) are analogous to those observed for **1a**. On the basis of their similar NMR spectra, we propose that **1a** and **1c(SP)** are square-pyramidal complexes analogous to structurally characterized **1b**. When the final sample is warmed to room temperature, the resonances for **1c(TBP)** and **1c(SP)** broaden while those for residual $^{13}C_2H_4$ and $^{13}CH_2{=}CH\text{-}t\text{-}Bu$ do not, a result that implies that **1c(TBP)** and **1c(SP)** interconvert intramolecularly on the NMR time scale but that olefins are not exchanging in and out of these tungstacycles rapidly. If the volatile components of the reaction shown in Scheme I are removed in vacuo, an approximately 50/50 mixture of **1c** and **1b** remains. Apparently, olefins exchange in and out of these tungstacycles on the *chemical* time scale, and since *tert*-butylethylene is much less volatile than ethylene, a considerable amount of **1b** is re-formed.

When $W(CH\text{-}t\text{-}Bu)(NAr)(OAr)_2$ is treated with $^{13}C_2H_4$ at 25 °C in toluene-d_8 and ^{13}C NMR spectra observed at -60 °C, an analogous mixture of TBP and SP forms of $W(^{13}CH_2{}^{13}CH_2{}^{13}CH_2)(NAr)(OAr)_2$ (**2c(TBP)** and **2c(SP)**, respectively, Table I) is observed. **2c(TBP)** and **2c(SP)** also interconvert intramolecularly on the NMR time scale at room temperature. $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ (**2b**)[7] can be isolated by treating $W(CH\text{-}t\text{-}Bu)(NAr)(OAr)_2$ with ethylene and *tert*-butylethylene and removing all volatile components in vacuo; it is a square pyramid (Table I) according to ^{13}C NMR spectra.

$W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ reacts with excess ethylene to give an initial α-t-Bu-substituted tungstacyclobutane complex **3a** that persists *for more than 10 h* at 25 °C before being converted to square-pyramidal $W(CH_2CH_2CH_2)(NAr)(O\text{-}t\text{-}Bu)_2$ (**3c**; eq 2, Table I) in the presence of



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[5] The compound crystallizes in the tetragonal system, space group $P4_2/n$ with Z = 8, a = 25.26 (2) Å, c = 9.720 (5) Å, V = 6202 Å^3, M_r = 711.48, ρ(calcd) = 1.524 g cm^{-3}, and μ = 40.05 cm^{-1}. Data were collected at -70 °C on a Rigaku AFC6R diffractometer equipped with a liquid-nitrogen low-temperature device and using Mo Kα radiation. The structure was solved by direct methods. Final R = 0.056 and R_w = 0.082. In the final cycles of least squares one of the alkoxide ligands was refined with isotropic thermal parameters and a CF_3 group held as a rigid group with fixed thermal parameters. All other portions of the molecule were well-behaved.

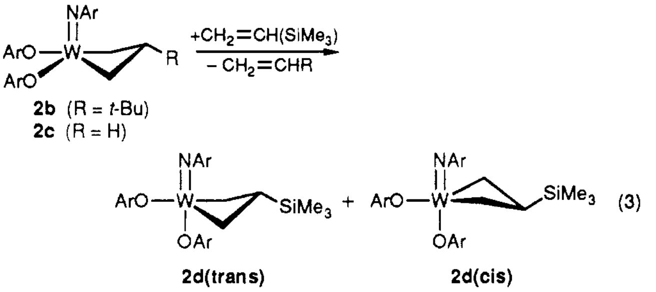
[6] The notation for a compound that contains ^{13}C labels will be idential with one that contains only naturally abundant ^{13}C.

[7] Ethylene (1.3 mmol) was added via vacuum transfer to a solution of 200 mg (0.255 mmol) of $W(CH\text{-}t\text{-}Bu)(NAr)(OAr)_2$ and 493 μL (3.83 mmol) of *tert*-butylethylene in 4.0 mL of pentane. After the solution had been stirred at 25 °C for 30 min, it was concentrated to a volume of $\sim$0.5 mL and cooled to -40 °C. **2b** (178 mg, 0.219 mmol, 86%) was isolated as a bright yellow, microcrystalline solid after the mother liquor was removed by pipette. Calcd for $WC_{43}H_{65}NO_2$: C, 63.62; H, 8.07. Found: C, 63.69; H, 8.05.

ethylene. **3a** clearly is more stable than **1a**; in the presence of excess ethylene **1a** rapidly gives **1c** and *tert*-butylethylene at temperatures above −20 °C. Square-pyramidal $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(O\text{-}t\text{-}Bu)_2$ (**3b**) can be prepared from **3a** and several equivalents of ethylene in the presence of a large excess of *tert*-butylethylene, but the reaction requires several hours at 25 °C.[8] Due to its extreme solubility in hydrocarbons, we have thus far been unable to isolate **3b** in pure form and in good yield.

The reaction between **2b** and ethylene to give **2c** and *tert*-butylethylene is zero-order in ethylene and first-order in tungsten between 9 and 34 °C with $\Delta H^{*} = 19.8\ (4)$ kcal mol^{-1}, $\Delta S^{*} = -6\ (1)$ eu,[9] and $\Delta G^{*}_{298} = 21.6\ (7)$ kcal mol^{-1}. These results strongly contrast with the relative stability of **3a** and **3b** toward loss of *tert*-butylethylene in the presence of ethylene to give **3c**.

The nature of the substituents on the metallacycle ligand also influences the metallacycle's core geometry. As shown in eq 3, addition of vinyltrimethylsilane to square-pyramidal **2b** or fluxional **2c** yields two *trigonal-bipyramidal* isomers according to NMR studies in an approximately 2:1 ratio that we assign as **2d(*trans*)** and **2d(*cis*)**.[10] The formation of two isomers can be rationalized on the basis of little difference in size between the axial NAr and axial OAr ligands.



2b (R = *t*-Bu)
2c (R = H)

2d(trans) **2d(cis)**

Our preliminary conclusions are that (i) the basic geometry of tungstacycles of this type sensitively depends upon the nature of the OR ligands and ring substituents and (ii) the barrier to interconversion of TBP and SP forms can be substantial. Detailed kinetic studies of these systems are now under way in order to determine how the core geometry of a tungstacyclobutane complex is related to its tendency to lose an olefin and to metathesize olefins. The results of these studies should be interesting to compare with those obtained for titanacyclobutane complexes where electron-donating substituents on the Cp ring stabilize the titanacycle and only the pseudotetrahedral core geometry is possible.[11]

Acknowledgment. R.R.S. thanks the National Science Foundation for research support (CHE 84-02892) and the U.S. Department of Energy, Division of University and Industry Programs, for funds to purchase the X-ray diffractometer (Grant DE-FG05-86ER75292). J.F. thanks the National Science Foundation for a predoctoral fellowship.

Registry No. **1a**, 121211-74-3; **1b**, 121211-75-4; **1c(SP)**, 121211-76-5; **1c(TBP)**, 121251-51-2; **2b**, 121211-77-6; **2c(SP)**, 121211-78-7; **2c(TBP)**, 121251-52-3; **2d(trans)**, 121211-82-3; **2d(cis)**, 121251-53-4; **3a**, 121211-79-8; **3b**, 121211-80-1; **3c**, 121211-81-2; $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2(CF_3)]_2$, 107440-83-5; $CH_2{=}CH(t\text{-}Bu)$, 558-37-2; C_2H_4, 74-85-1; $^{13}C_2H_4$, 51915-19-6; $W(CH\text{-}t\text{-}Bu)(NAr)(OAr)_2$, 109678-83-3; $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$, 107440-84-6; $CH_2{=}CH(SiMe_3)$, 754-05-2.

Supplementary Material Available: A completely labeled ORTEP drawing of $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ and tables of final positional and thermal parameters (3 pages); a listing of final observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

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[8] Ethylene (2.2 mmol) was added via vacuum transfer to a solution of 250 mg (0.434 mmol) of $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ and 1.40 mL (6.51 mmol) of *tert*-butylethylene in 3.0 mL of pentane. After the solution had been stirred at 25 °C for 23 h, it was concentrated to a volume of ~0.5 mL and cooled to −40 °C. The orange solid that precipitated was recrystallized a second time from minimal pentane at −40 °C to afford 73 mg (0.121 mmol, 28%) of **3b** as bright yellow solid.

[9] (a) A recent paper[9b] reported kinetic studies of related *cationic* five-coordinate tungstacyclobutane complexes prepared with norbornene.[9c] Rate-limiting ring opening was found to have essentially the same ΔS^{*} as that reported here. It is interesting to note that according to the chemical shifts of the ring carbon atoms in one metallacycle (152.5, 141.6, and 25.6 ppm[9c]) it would appear to be a trigonal bipyramid with all resonances shifted downfield in response to the positive charge. (b) Kress, J.; Osborn, J. A.; Amir-Ebrahimi, V.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1164. (c) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 899.

[10] A solution of 120 mg (0.148 mmol) of $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ (**2b**) and 107 μL (0.745 mmol) of vinyltrimethylsilane in 5 mL of pentane was stirred at 25 °C for 2 h. Volatiles were removed in vacuo to afford an orange foam which was recrystallized from pentane at −40 °C to afford 82 mg (0.099 mmol, 67%) of **2d** as a yellow powder. The same compound can also be prepared by adding ~3 equiv of ethylene to $W(CH\text{-}t\text{-}Bu)(NAr)(OAr)_2$, stirring the solution for 30 min at 25 °C, and then adding 5 equiv of vinyltrimethylsilane to the reaction mixture. For **2d(trans)**: $\delta(H_\alpha) = 4.87, 4.49$; $\delta(H_\beta) = -1.13$, $\delta(C_\alpha) = 100.5$, $\delta(C_\beta) = -0.99$. For **2d(cis)**: $\delta(H_\alpha) = 5.24, 4.20$; $\delta(H_\beta) = -1.23$, $\delta(C_\alpha) = 99.6$, $\delta(C_\beta) = -0.63$. Calcd for $WC_{42}H_{65}NO_2Si$: C, 60.93; H, 7.91. Found: C, 60.75; H, 7.95.

[11] (a) Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406. (b) Hawkins, J. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2821. (c) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

η^4-*s*-*trans*-1,3-Dienes as Ligands for Cationic Molybdenum Centers

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Summary: Reaction of $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_5Me_5)][BF_4]$ with $Me_3SiOCH{=}CHCH{=}CH_2$ affords [Mo{*endo*-*syn*-η^3-1-C_3H_4CHO}$(CO)_2(\eta^5\text{-}C_5Me_5)$], [Mo{*exo*-*syn*-$\eta^3$-1-$C_3H_4CHO$}$(CO)_2(\eta^5\text{-}C_5Me_5)$], and [Mo{*exo*-*anti*-$\eta^3$-1-$C_5H_4CHO$}$(CO)_2(\eta^5\text{-}C_5Me_5)$], which on treatment with the Wittig reagent Ph_3PCH_2 afford the corresponding η^3-pentadienyl complexes; protonation of both types of complexes at low temperature provides evidence for the formation of cationic η^4-*s*-*trans*-1,3-diene complexes.

The η^4-*s*-*cis*-1,3-diene ligand has played an important role in the development of organotransition-metal chemistry.[1] Recently, interest in 1,3-dienes as ligands has been further stimulated by the isolation and structural characterization of neutral complexes carrying η^4-*s*-*trans*-1,3-diene ligands.[2,3] Since it is likely that a different reactivity

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[1] *Principles and Applications of Organotransition Metal Chemistry*; Collman, J. P., Hegedus, L. S., Norton, J. R., Finke, R. G., Eds.; University Science Books: Mill Valley, CA, 1987.

[2] (a) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6433. (b) Nakamura, A.; Yasuda, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. (c) Erker, G.; Krüger, C.; Muller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1 and references therein. (d) Okamoto, T.; Yasuda, H.; Nakamura, Y.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 5008.

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