

Communications

***s*-trans-Diene Complexes of a First-Row Transition Metal.
Half-Sandwich *s*-trans- η^4 -1,3-Diene Nitrosyl Complexes of
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Received October 3, 2005

Summary: The first *s*-trans-1,3-diene complexes of a first-row transition metal have been prepared and characterized both in solution and in the solid state. The unexpected *s*-trans configuration was obtained from photolytic decarbonylation of Cp'Cr(NO)(CO)₂ (Cp' = η^5 -C₅H₅ and η^5 -C₅Me₅) in the presence of conjugated dienes. Related η^2 -olefin and η^2 -2-alkyne complexes have also been prepared.

Although *s*-trans- η^4 -diene complexes of the transition metals have been known for a quarter century,^{1–4} none have been reported for the first-row transition metals.⁵ *s*-trans-Diene complexes of the second- and third-row transition metals are unusually reactive and undergo a range of interesting transformations, participating readily in migratory insertion processes² and reacting with both Brønsted acids^{4c} and strong Lewis acids, the latter to generate zwitterionic olefin polymerization catalysts.² Installation of *s*-trans-diene functionality on a first-row metal, assuming it is possible to do so, is expected to provide very high, and perhaps unique, reactivity. Here we report general

methodology for the preparation of unprecedented *s*-trans-diene complexes supported by the half-sandwich chromium nitrosyl fragment, (C₅R₅)CrNO(*s*-trans- η^4 -1,3-diene) (R = H, Me), analogous to the more familiar second-^{4a} and third-row^{4b} congeners. Chromium η^4 -1,3-diene complexes are relatively common, but all previously reported chromium diene ligands exclusively adopt the *s*-cis configuration.⁶

The synthesis of chromium diene complexes in this series is complicated by the inherent instability of complexes of the form [(C₅H₅)Cr(NO)X₂]₂ (X = halide, alkyl),⁷ demanding an alternative strategy to those used for molybdenum and tungsten. Photolytic carbonyl substitution has been previously demon-

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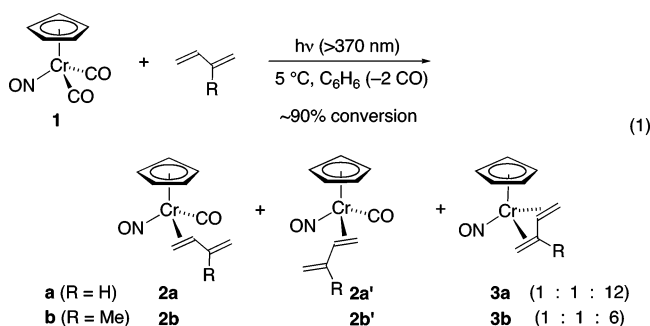
(3) Fukumoto, H.; Mashima, K. *Organometallics* **2005**, *24*, 3932–3938.

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(5) Computational analysis of *s*-cis- and *s*-trans-diene coordination: (a) Tatsumi, K.; Yasuda, H.; Nakamura, A. *Isr. J. Chem.* **1983**, *23*, 145–150. (b) Hunter, A. D.; Legzdins, P.; Einstein, F. W. B.; Willis, A. C.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1986**, *108*, 3843–4844. (c) See also ref 4d.

strated for $(C_5H_5)CrNO(CO)_2$, **1**, providing η^2 -alkene and η^2 -alkyne complexes, although no evidence for a second carbonyl substitution has been obtained.^{8,9} Unfortunately, however, the initial substitution products remain photolabile; reactions can be run only to low conversions and provide impractically low isolated yields. No previous investigation of photochemical substitution using conjugated dienes has been reported for this system.

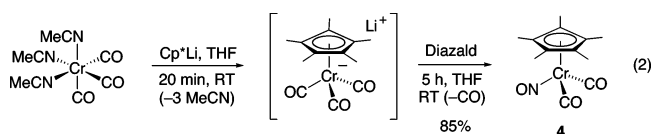
Photolysis of $(C_5H_5)CrNO(CO)_2$ (**1**) in the presence of butadiene (450 W Hanovia Hg, 5 °C) proceeds to give mixtures of η^2 -diene complexes **2** and the desired η^4 -diene complex **3**, from single and double decarbonylation, respectively.¹⁰ Concomitant decomposition is also observed, resulting in extensive plating of the photolysis apparatus and unacceptably low isolated yields. The decomposition of the η^2 -diene complex **2** is substantially faster than loss of the η^4 -diene **3**; in this way, the η^4 -diene complex **3** can be isolated in very pure form, albeit in very low yield.



After extensive optimization, however, conditions for the high-yield synthesis of η^4 -diene complexes have been determined. Photolytic decomposition is completely suppressed under ultraviolet irradiation through a 370 nm cutoff filter, leading, in the presence of excess butadiene, to an inseparable mixture of $CpCrNO(CO)(\eta^4$ -*s-trans*-butadiene) complex **3a**, accompanied by only minor amounts of the intermediate $CpCrNO(CO)(\eta^2$ -butadiene) **2a/2a'**, obtained as a mixture of two structurally ambiguous diastereomers (eq 1).¹⁰ Qualitatively similar results are observed upon photolysis in the presence of isoprene,

providing $CpCrNO(CO)(\eta^4$ -*s-trans*-2-methylbutadiene) complex **3b** in reasonable selectivity. Although the conversion is excellent (~90%), the reactions cannot be driven exclusively to the η^4 -diene. Unfortunately, neither the η^2 -diene nor η^4 -diene product is indefinitely stable at room temperature as an isolated solid and both suffer diene loss under prolonged vacuum. Nonetheless, infrared analysis of the isolated η^4 -butadiene complex **3a** in THF shows a single nitrosyl band at 1670 cm^{-1} and no observable carbonyl absorption. NMR spectroscopy unambiguously establishes the *s-trans* configuration of the butadiene ligand: all six butadiene hydrogens appear as chemically inequivalent resonances, inconsistent with the higher symmetry of the *s-cis*-diene complex.

Photolytic diene substitution in the corresponding pentamethylcyclopentadienyl series is more straightforward, producing *s-trans*-diene complexes of greater kinetic and thermodynamic stability. Although the preparation of $(C_5Me_5)CrNO(CO)_2$ (**4**) from chromium hexacarbonyl is inconveniently slow and low-yielding (48%),¹¹ a substantial reduction in reaction time and increase in isolated yield can be realized by starting from the more labile tricarbonylchromium tris(acetonitrile) complex (eq 2).¹² In this way, the addition of C_5Me_5Li is complete in less than 20 min at room temperature, and the subsequent nitrosylation produces complex **4** in 85% yield after isolation and purification.¹³



Photolysis of complex **4** in the presence of excess butadiene leads exclusively to the formation of *s-trans*- η^4 -butadiene complex **5a** (eq 3), isolated cleanly and in high yield after filtration through silica gel and crystallization. The UV cutoff filter is superfluous in this series: no decomposition or plating is observed even after prolonged photolysis through Pyrex glassware (> 36 h). Similarly, substituted *s-trans*- η^4 -complexes **5b** and **5c** can be prepared by photolysis in the presence of isoprene and 2,3-dimethylbutadiene, respectively (eq 3).¹⁴ Complexes **5a** and **5b** are formed as single isomers, as revealed by NMR spectroscopy, whereas complex **5c** is formed as a 9:1 mixture of isomers. Although NMR spectroscopy establishes that the η^4 -diene configuration in complex **5a** and the major isomer of **5c** is *s-trans*, insufficient information is obtained from the NMR spectrum to assign the configuration of the complex **5b** (vide infra).¹⁰ The minor isomer of **5c** is tentatively assigned the *s-cis* configuration on the basis of chemical shifts very similar to the known *s-cis*-dimethylbutadiene complex of molybdenum.^{4b} No isomerization is observed in solution at room temperature, suggesting, perhaps surprisingly, that the *s-trans* isomers may be thermodynamically favored, similar to the more familiar molybdenum analogues.¹⁵ Analysis of aliquots taken

(6) (a) $(C_4H_8NC_5Me_4)Cr(PMe_3)(C_4H_6)$: Döhring, A.; Göhre, J.; Jolly, P. W.; Kryger, B.; Rust, J.; Verhovnik, G. P. *J. Organometallics* **2000**, *19*, 388–402. $Cp^*Cr(CO/PR_3)_2$ (diene): Betz, P.; Döhring, A.; Emrich, R.; Goddard, R.; Jolly, P. W.; Krüger, C.; Romão, C.; Schönfelder, K. U.; Tsay, Y.-H. *Polyhedron* **1993**, *12*, 2651–2662. (b) $Cr(CO)_3(P(OR)_3)(C_4H_6)$: Wang, N.-F.; Wink, D. J.; Dewan, J. C. *Organometallics* **1990**, *9*, 335–340. Kreiter, C. G.; Özkar, S. *J. Organomet. Chem.* **1978**, *152*, C13–C18. (c) $Cr(CO)_4$ (diene): Kotzian, M.; Kreiter, C. G.; Özkar, S. *J. Organomet. Chem.* **1982**, *229*, 29–42. Fischler I.; Budzwait, M.; Koerner von Gustorf, E. A. *J. Organomet. Chem.* **1976**, *105*, 325–330. Koerner von Gustorf, E. A.; Jaenicke, O.; Wolfbeis, O.; Eady, C. R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 278–286. Koerner von Gustorf, E. A.; Jaenicke, O.; Polansky, O. E. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 532–533. (d) $Cr(dmpe)(CO)_2$ (diene): Kreiter, C. G.; Kotzian, M. *J. Organomet. Chem.* **1985**, *289*, 295–308. (e) Review: Kreiter, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297–375.

(7) Reduction of the Cr(I) dimer $[CpCr(NO)]_2$ ^{7a} or the anionic complex $[CpCr(NO)]_2^-$ ^{7b} in the presence of diene failed to yield tractable products. (a) Legzdins, P.; Nurse, C. R. *Inorg. Chem.* **1985**, *24*, 327–332. (b) Legzdins, P.; McNeil, W. S.; Rettig, S. J.; Smith, K. M. *J. Am. Chem. Soc.* **1997**, *119*, 3513–3522.

(8) (a) Herberhold, M.; Alt, H.; Kreiter, C. G. *Liebigs Ann. Chem.* **1976**, 300–316. (b) Herberhold, M.; Alt, H.; Kreiter, C. G. *J. Organomet. Chem.* **1972**, *42*, 413–418. (c) Herberhold, M.; Alt, H. *J. Organomet. Chem.* **1972**, *42*, 407–412.

(9) Photolyses in the presence of nonconjugated dienes^{8a} leads to the formation of tethered binuclear bis(monoolefin) complexes, suggesting that the remaining CO ligand resists photolytic labilization.

(10) Experimental details and characterization data are provided as Supporting Information.

(11) Malito, J. T.; Shakir, R.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1980**, 1253–1258.

(12) Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433–434.

(13) This procedure can also be used to obtain $(C_5H_5)CrNO(CO)_2$ in improved yield (90%), starting from sodium cyclopentadienide.

(14) The duration of photolysis required for high conversion is highly dependent on the scale of the reaction, increasing proportionally with increasing scale.

(15) The coordination of conformationally rigid *s-cis*-dienes is currently under investigation. Preliminary spectroscopic evaluation of the reactions of simple cycloalka-1,3-dienes suggests that this system, oddly, resists the formation *s-cis*- η^4 -diene complexes, instead producing bis(η^2 -coordinated) bimetallic complexes!

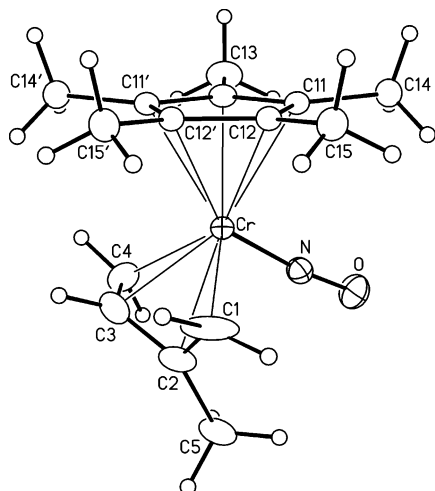


Figure 1. Solid-state molecular structure of *s-trans*-isoprene complex **5b**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Selected bond lengths (Å) and angles (deg): Cr–N = 1.679(8), O–N = 1.208(9), Cr–C(1) = 2.188(4), Cr–C(2) = 2.146(6), Cr–C(3) = 2.080(6), Cr–C(4) = 2.245(12), C(1)–C(2) = 1.417(14), C(2)–C(3) = 1.356(11), C(2)–C(5) = 1.507(12), C(3)–C(4) = 1.317(15); Cr–N–O = 173.5(12), N–Cr–C(1) = 101.6(6), N–Cr–C(2) = 88.0(4), N–Cr–C(3) = 108.3(4), N–Cr–C(4) = 92.6(3), C(1)–C(2)–C(3) = 112.7(8), C(1)–C(2)–C(5) = 124.1(12), C(3)–C(2)–C(5) = 122.7(10), C(2)–C(3)–C(4) = 121.7(8).

throughout the reaction of complex **4** with butadiene shows minor spectroscopic signatures consistent with the formation of a transient η^2 -butadiene intermediate **II'** (eq 3), formed as an approximately 1:1 mixture of unassigned diastereomers.¹⁰

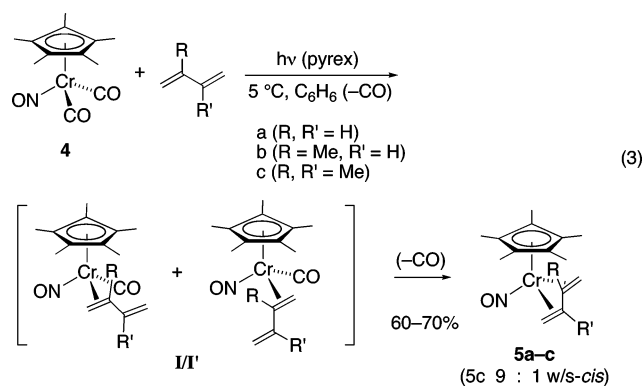


Figure 2. Solid-state molecular structure of *s-trans*-2,3-dimethylbutadiene complex **5c**. Hydrogen atoms of the Cp* ligand are omitted. Selected bond lengths (Å) and angles (deg): Cr–N = 1.667(3), O–N = 1.212(3), Cr–C(1) = 2.222(3), Cr–C(2) = 2.163(3), Cr–C(3) = 2.135(3), Cr–C(4) = 2.235(3), C(1)–C(2) = 1.386(4), C(2)–C(3) = 1.448(4), C(3)–C(4) = 1.401(5), C(2)–C(5) = 1.509(4), C(3)–C(6) = 1.513(4); Cr–N–O = 172.6(3), N–Cr–C(1) = 101.36(13), N–Cr–C(2) = 88.58(12), N–Cr–C(3) = 108.05(12), N–Cr–C(4) = 89.37(13), C(1)–C(2)–C(3) = 116.7(3), C(1)–C(2)–C(5) = 121.1(3), C(3)–C(2)–C(5) = 121.6(3), C(2)–C(3)–C(4) = 118.4(3), C(2)–C(3)–C(6) = 120.4(3), C(4)–C(3)–C(6) = 120.8(3).

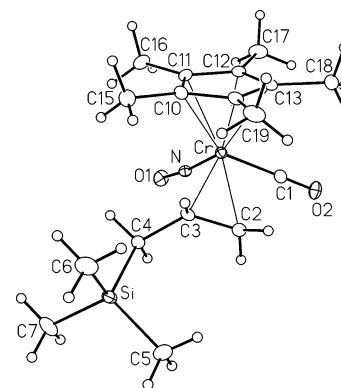


Figure 3. Solid-state molecular structure of the η^2 -allyltrimethylsilane complex **6b/6b'**. Selected bond lengths (Å) and angles (deg): Cr–N = 1.676(2), O(1)–N = 1.198(3), Cr–C(1) = 1.856(3), O(2)–C(1) = 1.149(3), Cr–C(2) = 2.214(3), Cr–C(3) = 2.206(3), C(2)–C(3) = 1.380(4), C(3)–C(4) = 1.508(4); Cr–N–O(1) = 173.0(2), Cr–C(1)–O(2) = 178.2(3), N–Cr–C(1) = 92.77(12), N–Cr–C(2) = 102.09(12), N–Cr–C(3) = 93.77(11), C(2)–C(3)–C(4) = 122.9(3).

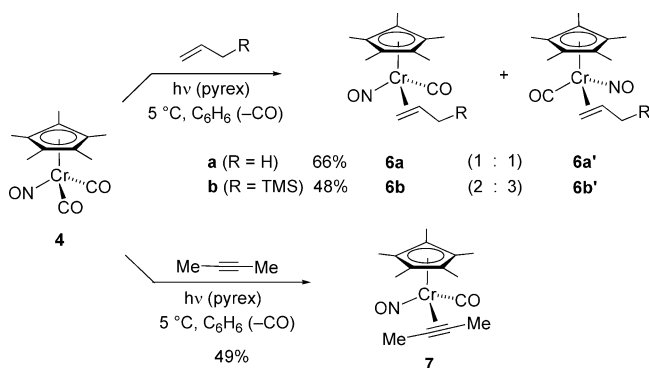
otherwise unremarkable, consistent with *s-trans*-diene complexes of both molybdenum and zirconium.^{1–4}

Consistent with the reactivity of the parent (cyclopentadienyl)-chromium system,^{8,9} (C₅Me₅)CrNO(CO)₂ (**4**) is strongly resistant to double carbonyl substitution in the presence of either simple alkenes or nonconjugated dienes (e.g., 1,5-hexadiene), leading to monosubstitution products only, even upon prolonged photolysis in the presence of excess alkene. Thus, photolysis of dicarbonyl complex **4** in the presence of a large excess of propene or allyltrimethylsilane provides η^2 -alkene complexes **6a** and **6b**, respectively, each as a mixture of otherwise unassigned diastereomers (Scheme 1). Spectroscopic analysis clearly reveals that one diastereomer of each complex is fluxional at room temperature, broadening many of the associated signals in both ¹H and ¹³C NMR spectra and obscuring most of the correlations in the two-dimensional spectra. At –80 °C, however, both diastereomers of propene complex **6a** are static, with all resonances and correlations clearly resolved.¹⁰

Single crystals of all three η^4 -diene complexes **5** were analyzed by X-ray crystallography. Although the structure of butadiene complex **5a** was complicated by an unresolvable degree of disorder, the solid-state molecular structures of both η^4 -isoprene and η^4 -dimethylbutadiene complexes **5b** and **5c** have been determined to high resolution (Figures 1 and 2).¹⁶ The diene orientation in each complex is significantly distorted, but clearly *s-trans*, displaying typical dihedral torsion angles of 125.2(11)° and 119.3(3)°, respectively.¹⁰ The structures appear

(16) (a) Crystal data for complex **5b** (C₁₅H₂₃CrNO, –80 °C): orthorhombic, *Pnma* (No. 62), *a* = 9.6520(10) Å, *b* = 12.3096(12) Å, *c* = 12.1615(12) Å, *V* = 1444.9(3) Å³, *Z* = 4, ρ_{calcd} = 1.312 g cm^{–3}, μ = 0.78 mm^{–1}, *R*₁ = 0.0418, *wR*₂ = 0.1212 [*F*_o² ≥ –3 σ (*F*_o²)]. (b) Crystal data for complex **5c** (C₁₆H₂₅CrNO, –80 °C): monoclinic, *P2₁/c* (No. 14), *a* = 8.5929(7) Å, *b* = 23.7465(19) Å, *c* = 8.5735(7) Å, β = 116.8897(11)°, *V* = 1560.3(2) Å³, *Z* = 4, ρ_{calcd} = 1.274 g cm^{–3}, μ = 0.726 mm^{–1}, *R*₁ = 0.0466, *wR*₂ = 0.1376 [*F*_o² ≥ –3 σ (*F*_o²)].

Scheme 1



In solution at room temperature, both η^2 -alkene complexes **6a** and **6b** suffer from slow dissociation of the alkene. Nonetheless, crystallization proceeds at low temperature without notable decomposition and, for allylsilane complex **6b**, delivers single crystals comprising a single diastereomer. The structure of this complex has been determined by X-ray crystallography (Figure 3).¹⁷

Photolysis of dicarbonyl complex **4** in the presence of excess 2-butyne similarly provides only the η^2 -2-butyne complex **7**, isolated in modest but reasonable yield. The relatively upfield alkyne resonances in the ¹³C NMR spectrum are consistent with the presence of a simple two-electron, π -coordinated alkyne.^{18,19} For both alkene and alkyne substrates, the complete absence of double substitution products remains poorly understood.

(17) Crystal data for complex **6b/6b'** (C₁₇H₂₉CrNO₂Si, -80 °C): monoclinic, *P*2₁/*n* (an alternate setting of *P*2₁/*c* [No. 14]), *a* = 12.3077(15) Å, *b* = 13.0033(15) Å, *c* = 12.7883(15) Å, β = 106.697(2)°, *V* = 1960.4(4) Å³, *Z* = 4, ρ_{calcd} = 1.218 g cm⁻³, μ = 0.651 mm⁻¹, *R*₁ = 0.0473, *wR*₂ = 0.1165 [*F*_o² ≥ -3σ(*F*_o²)].

(18) Photolysis under an atmosphere of acetylene also provides a simple η^2 -alkyne (rather than vinylidene) product, as determined by preliminary spectroscopic analysis.^{10,19} We have as yet been unable to isolate this product as a pure compound.

(19) Templeton, J. *Adv. Organomet. Chem.* **1989**, 29, 1–100.

The unexpected preference for *s-trans* coordination of conjugated dienes is, among first-row transition metals, unique to chromium and, among chromium η^4 -diene complexes,⁶ unique to this particular half-sandwich nitrosyl coordination sphere. The mere existence of *s-trans*-diene coordination in the first transition series constitutes a provocative challenge to standard structural paradigms. This investigation, however, clearly reveals that there exists no overriding electronic or steric prohibition on accommodating *s-trans*-coordination in the first transition series. The role of relative electron deficiency in promoting *s-trans* over *s-cis* coordination, as articulated by Legzdins^{5b} and more recently discussed by Mashima and Nakamura,^{2c} provides a compelling and rational basis for the discovery of *s-trans*-1,3-diene coordination elsewhere among the first-row transition metals.

For the moment, however, a *specific* rationale for *s-trans*-diene coordination in (cyclopentadienyl)chromium nitrosyl complexes remains elusive, warranting further experimental and computational investigation. Structural issues notwithstanding, *s-trans*-diene complexes of this nominally zerovalent and carbonyl-free chromium system are expected to exhibit a range of interesting and, perhaps, unique reactivity. The results of this ongoing investigation will be reported in due course.

Acknowledgment. The authors thank Professor Josef Takats for providing assistance with photochemical equipment. Financial support from the Natural Sciences and Engineering Research Council (NSERC) of Canada and the University of Alberta is gratefully acknowledged.

Supporting Information Available: Details of the one- and two-dimensional NMR spectroscopy and assignments for complexes **2–7**; details of the X-ray structure determinations for complexes **5b**, **5c**, and **6b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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