5), a product clearly inconsistent with kinetic central carbon alkylation and subsequent rearrangement.

The site of kinetic nucleophilic addition in this system is thus dependent on the coordination geometry of the crotyl ligand. It is not yet possible, however, to completely isolate the electronic effects of allyl configuration from the steric effects of substituent stereochemistry; unfortunately, neither the exo, anti crotyl nor the unsubstituted endo allyl complex can be prepared by standard methods. Both exo and endo configurational isomers of the structurally analogous $[(C_5Me_5)Ir(C_2H_4)(\eta^3\text{-allyl})]^+OTf^-$ react with strong nucleophiles to give metallacyclobutane complexes exclusively,[1b,12] but the comparison is acutely limited by the electronic differences in the ancillary ligand. The strong donor phosphine is expected to accentuate differences in coordination geometry and electron distribution in the isomeric allyl complexes, requiring a combination of crystallography, molecular orbital calculations,[13] and molecular mechanics to provide the insight necessary to rationalize the observed reactivity.

Acknowledgment. Financial support from the National Science Foundation, the NIH-BRSG program, a Union Carbide Innovation Recognition Award, and an American Cyanamid Faculty Award is gratefully acknowledged. We thank Johnson Matthey, Inc., for a generous loan of precious metals.

Supplementary Material Available: Spectroscopic and analytical data (including difference NOE spectra) for complexes 1-8 (5 pages). Ordering information is given on any current masthead page or may be obtained by writing directly to J.M.S.

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[12] The overriding kinetic preference for metallacyclobutane formation in the iridium system is observed despite significant differences noted in the electrophilicity of potential reaction sites in the two isomers. A pronounced configuration dependence in this system for the addition of softer "nonkinetic" nucleophiles has, in fact, been noted.[1b]

[13] This degree of subtlety in reactivity is not readily accommodated by current theoretical treatments of the regioselectivity issue: (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047. Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Vol. 1, pp 897-937. (b) Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.

Photoinduced [6 + 2] Cycloadditions of Alkynes to Tricarbonyl(cycloheptatriene)chromium(0)

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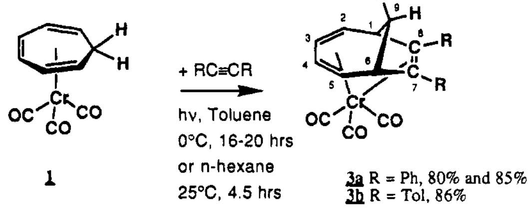
Summary: Photolysis of $[(\eta^6\text{-}C_7H_8)Cr(CO)_3]$ (**1**) and RC≡CR (**2a**, R = Ph; **2b**, R = Tol) in toluene or *n*-hexane results in the formation of $[(\eta^2{:}\eta^4\text{-}C_9H_8R_2)Cr(CO)_3]$ (**3a,b**) in 70-85% isolated yield via a [6 + 2] cycloaddition reaction. Heating **3a,b** in toluene gives the bicyclo[4.2.1]nona-2,4,7-trienes **4a,b** and $[(\eta\text{-}C_6H_5Me)Cr(CO)_3]$. Photolysis of **1** and excess DMAD (dimethyl acetylenedicarboxylate, **5**) in toluene at 0 °C yields the bicyclotriene **4c** as the major product and small amounts of the arene $C_6(CO_2Me)_6$ and the [4 + 2] cycloadduct between **4c** and **5**.

Transition-metal-mediated higher order ([6 + 2], [4 + 4], and [6 + 4]) cycloaddition reactions have been demonstrated by a number of groups[1] and show a high selectivity for the higher order process over the competing [4 + 2] process. For example, Rigby and co-workers have recently reported that photolysis of solutions of $[(\eta^6\text{-}C_7H_8)Cr(CO)_3]$ (1) and electron-deficient olefins leads to good yields of functionalized bicyclo[4.2.1]nona-2,4-dienes.[1a] Titanium-catalyzed [6 + 2] cycloadditions of bulky internal alkynes to cyclohepta-1,3,5-triene have also been reported,[1f,g] although the scope of this reaction is limited by a competing cyclotrimerization of the trienophile when smaller alkyne substituents are present. We now report photoinduced [6 + 2] cycloadditions between $[(\eta^6\text{-}C_7H_8)\text{-}Cr(CO)_3]$ (1) and alkynes that lead to complexes of bicyclo[4.2.1]nona-2,4,7-trienes as well as the free organic species.

Photolysis (450-W Conrad-Hanovia medium-pressure Hg vapor lamp, Pyrex glassware) of toluene solutions of 1 and 1 equiv of the alkynes RC≡CR (**2a**, R = Ph; **2b**, R = Tol) at 0 °C for 16-20 h resulted in a gradual disappearance of 1, as monitored by IR spectroscopy, and formation of $[(\eta^2{:}\eta^4\text{-}C_9H_7R_2)Cr(CO)_3]$ (**3a**, R = Ph; **3b**, R = Tol) (eq 1).



(1)

Complexes **3a,b** were isolated as analytically pure deep red crystalline solids in 80% and 86% yields, respectively, and characterized using IR, ^1H NMR, and ^{13}C NMR

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[1] (a) Rigby, J. H.; Henshilwood, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 5122. (b) Rigby, J. H.; Ateeq, H. S. *J. Am. Chem. Soc.* **1990**, *112*, 6442. (c) Kreitner, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297-375 and references therein. (d) Davis, R. E.; Dodds, T. A.; Hseu, T.-H.; Wagnon, J. C.; Devon, T.; Tancrede, J.; Mckennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 7562. (e) Nagashima, H.; Matsuda, H.; Itoh, K. *J. Organomet. Chem.* **1983**, *258*, C15. (f) Mach, K.; Antropiusova, H.; Petrusova, L.; Hanus, V.; Turecek, F.; Sedmera, P. *Tetrahedron* **1984**, *40*, 3295. (g) Mach, K.; Antropiusova, H.; Sedmera, P.; Hanus, V.; Turecek, F. *J. Chem. Soc., Chem. Commun.* **1983**, 805. (h) Bourner, D. G.; Brammer, L.; Green, M.; Moran, G.; Orpen, A. G.; Reeve, C.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1409.

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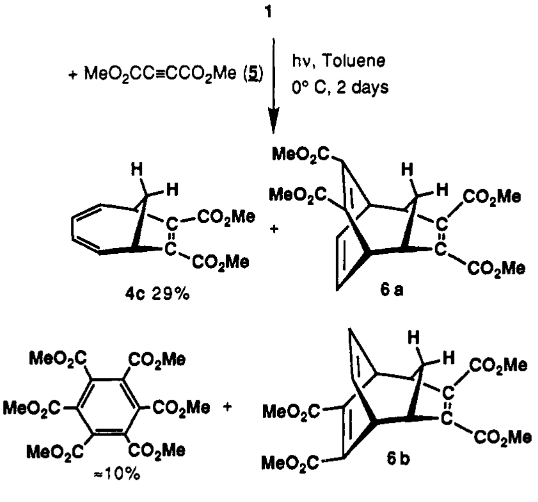
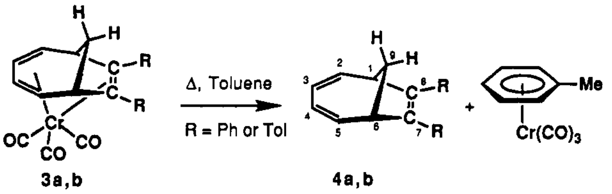
Scheme I



spectroscopy.[2] In *n*-hexane at room temperature the cycloaddition proceeds more rapidly (4.5 h) and **3a** precipitates as red crystals in excellent yield (85%). In addition, a small amount of chromium hexacarbonyl (observed by IR) and 7,8-diphenylbicyclo[4.2.1]nona-2,4,7-triene (**4a**; detected using GCMS) are also present, presumably due to partial decomposition of **3a**.

The products **3a,b** are thermally stable in nonaromatic solvents or as solids; however, they react with toluene at elevated temperatures (>80 °C) to give tricarbonyl(toluene)chromium(0) and the bicyclo[4.2.1]nona-2,4,7-trienes (**4a,b**). The trienes can be isolated following chromatography (TLC, silica) as white crystalline solids and were spectroscopically characterized[3] (eq 2).



(2)

In contrast to the reactions in toluene and *n*-hexane, photolysis of THF solutions of **1** and **2a** gave **4a** in poor yield (17%) and no isolable organometallic species. Monitoring of the reaction by IR spectroscopy did, however, show a highly unstable carbonyl-containing compound is present.[4]

The reaction of DMAD (**5**) with **1** under similar conditions also leads to a [6 + 2] cycloaddition between the alkyne and cycloheptatriene. Thus, photolysis of excess **5** (5 equiv) and **1** in toluene gave the bicyclononatriene **4c** (R = CO_2Me, 29%)[5] along with small amounts of the arene $C_6(CO_2Me)_6$ and two isomers (**6a,b**) of the [4 + 2] cycloadduct between **4c** and **5**[5] (Scheme I). Use of 1 equiv of **5** gave **4c** in poor yield, with prolonged photolysis leading to decomposition of **1**.

A possible mechanism for the formation of **3a,b**, also proposed for [6 + 2] cycloadditions between $[(\eta^4\text{-}C_7H_8)Fe(CO)_3]$ and suitable trienophiles,[1d] is as follows. Initial photolysis leads to either CO or partial (η^6 to η^4) cycloheptatriene decomplexation followed by coordination of the alkyne. Alkyne insertion into the Cr–C(1) and Cr–C(6) bonds and recomplexation of the olefin or CO would then give **3**. The role of the solvent in the formation of both **3** and **4** can be rationalized as follows. In toluene and *n*-hexane the intermediate 16-electron photoproduct can be trapped by the alkyne, allowing the cycloaddition to proceed in good yield. However, in a coordinating solvent such as THF, competition between the alkyne and solvent for the vacant coordination site at the metal reduces the efficiency of the reaction.

The formation of small amounts of the arene $C_6(CO_2Me)_6$ when **5** is used is consistent with results reported by Mach et al.[1f] in the reactions of non sterically demanding alkynes with titanium catalysts. However, the observation of a [6 + 2] cycloadduct between **5** and cycloheptatriene as a major product, with only small amounts of cyclotrimerization products, is new[6] and demonstrates that the use of a coordinated triene in **1** greatly facilitates [6 + 2] cycloadditions with alkynes. Further studies to investigate the generality of the reaction with terminal and non sterically demanding alkynes, as well as other trienophiles, are in progress.

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Supplementary Material Available: Textual description of selected experimental procedures for the preparation of compounds **3** and **4** (2 pages). Ordering information is given on any current masthead page.

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[2] **3a**: Anal. Calcd for $C_{24}H_{18}CrO_3$: C, 70.93; H, 4.46. Found: C, 70.91; H, 4.26. IR (hexane): ν(CO) 1978, 1913, 1887 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 0.91 (1 H, d, $J_{H_{9'}H_9}$ = 11.9 Hz, $H_{9'}$), 1.74 (1 H, m, H_9), 3.93 (2 H, t, $J_{H_2H_3}$, $J_{H_5H_4}$ = 6.7 Hz, $J_{H_2H_1}$, $J_{H_5H_6}$ = 6.7 Hz, $H_{2,5}$), 4.42 (2 H, m, $H_{1,6}$), 5.20 (2 H, dd, $J_{H_3H_2}$, $J_{H_4H_5}$ = 6.7 Hz, $J_{H_3H_1}$, $J_{H_4H_6}$ = 3.0 Hz, $H_{3,4}$), 7.25 (6 H, m, Ph), 7.59 (4 H, m, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 33 (C_9), 47 (C_1, C_6), 68.5 (C_2, C_5), 89.8 ($C_{7,8}$), 96 ($C_{3,4}$), 124–135 (Ph), 228, 232, 233 (CO). **3b**: Anal. Calcd for $C_{26}H_{22}CrO_3$: C, 71.88; H, 5.10. Found: C, 72.08; H, 5.00. IR (hexane): ν(CO) 1979, 1913, 1887 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 0.88 (1 H, d, $J_{H_{9'}H_9}$ = 11.6 Hz, $H_{9'}$), 1.69 (1 H, q, $J_{H_9H_{9'}}$ = 11.6 Hz, $J_{H_9H_{1,6}}$ = 5.2 Hz, H_9), 2.33 (6 H, s, CH_3), 3.86 (2 H, t, $J_{H_2H_3}$, $J_{H_5H_4}$ = 7.0 Hz, $J_{H_2H_1}$, $J_{H_5H_6}$ = 7.0 Hz, $H_{2,5}$), 4.37 (2 H, m (brd), $H_{1,6}$), 5.17 (2 H, dd, $J_{H_3H_2}$, $J_{H_4H_5}$ = 7.0 Hz, $J_{H_3H_1}$, $J_{H_4H_6}$ = 2.0 Hz, $H_{3,4}$), 7.07 (4 H, d, J = 8.0 Hz, C_6H_4Me), 7.45 (4 H, d, J = 8.0 Hz, C_6H_4Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 21.2 (C_6H_4Me), 33.1 (C_9), 47.3 (C_1, C_6), 69.3 (C_2, C_5), 89.3 ($C_{7,8}$), 96.7 ($C_{3,4}$), 124–135 (C_6H_4Me), 228, 232, 233 (CO).

[3] Spectral data for **4a** were identical with those reported in ref 1d. **4b**: ^1H NMR ($CDCl_3$, δ) 1.81 (1 H, d, $J_{H_{9'}H_9}$ = 11 Hz, $H_{9'}$), 2.31 (6 H, s, CH_3), 2.58 (1 H, m, $J_{H_9H_{9'}}$ = 11 Hz, $J_{H_9H_{1,6}}$ = 7 Hz, H_9), 3.62 (2 H, t, $J_{H_1H_2}$, $J_{H_6H_5}$ = 7 Hz, $J_{H_1H_9}$, $J_{H_6H_9}$ = 7 Hz, $H_{1,6}$), 5.88 (2 H, dt, $H_{2,5}$), 6.28 (2 H, m, $H_{3,4}$), 6.98 (4 H, d, J = 8.0 Hz, C_6H_4Me), 7.09 (4 H, d, J = 8.0 Hz, C_6H_4Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 21.1 (C_6H_4Me), 30.4 (C_9), 49.3 (C_1, C_6), 124.5, 129.0, 133.9, and 136.2 (C_6H_4Me), 128.8 (C_2, C_5), 135.5 (C_7, C_8), 139.6 (C_3, C_4); MS *m/e* 298 (M^+), 283 (M^+ – Me), 268, 253, intensity 100 peak at 91.

[4] Repeated attempts to isolate this unstable product failed. Its IR spectrum monitored during the reaction was ν(CO) 1937 and 1895 cm^{-1}. The complex decomposes upon removal of THF in vacuo and shows no ν(CO) bands in other solvents.

[5] Isolated yield for **4c**. The yield for $C_6(CO_2Me)_6$ is estimated from GCMS of the reaction mixture. Compounds **6a,b** are isolated as a mixture in <5% yield. **4c**: ^1H NMR ($CDCl_3$, δ) 1.55 (1 H, d, $J_{H_{9'}H_9}$ = 12 Hz, $H_{9'}$), 2.26 (1 H, m, H_9), 3.50 (2 H, t, $J_{H_1H_2}$, $J_{H_6H_5}$ = 7 Hz, $J_{H_1H_9}$, $J_{H_6H_9}$ = 7 Hz, $H_{1,6}$), 3.69 (6 H, s, Me), 5.90 (2 H, m, $H_{2,5}$), 6.10 (2 H, m, $H_{3,4}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 29.5 (C_9), 44.7 (Me), 52.0 (C_1, C_6), 125.8 (C_2, C_5), 132.5 (C_7, C_8), 136.5 (C_3, C_4), 165.2 (CO); MS *m/e* 234 (M^+), 218 (M^+ – Me), 202, 173, 115 (100, M^+ – $2CO_2Me$). **6a,b**: ^1H NMR ($CDCl_3$, δ) 1.68 and 1.81 (2 H, d, $H_{9'}$), 2.28 and 2.42 (2 H, m, H_9), 3.13 and 3.27 (4 H, t, $H_{1,6}$), 3.6 and 3.72 (12 H, s, Me), 3.8–4.0 (4 H, m, $H_{2,4}$), 5.67 and 5.84 (4 H, m, $H_{3,4}$); MS *m/e* 375 (M^+ – H), 344, 285, 256, 59 (100, CO_2Me).

[6] A [6 + 2] cycloadduct between DMAD and $[(\eta^4\text{-}C_7H_8)Fe(CO)_3]$ has been reported in ref 1d (10% yield), but no organic species was isolated.