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Metal-Mediated [6 + 2] Cycloadditions of Alkynes to Cycloheptatriene and *N*-Carbethoxyazepine

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Abstract: UV photolysis of $[(\eta^6\text{-}C_7H_7R)Cr(CO)_3]$ (**1**, R = H, Ph, $CH\{CO_2Me\}_2$) and $R'C\equiv CR'$ (R' = Ph, Tol, $SiMe_3$, Et) in toluene or *n*-hexane gives the [6 + 2] cycloadducts $[(\eta^{2:4}\text{-}C_9H_7\{R\}R'_2)Cr(CO)_3]$ (**2**). Heating **2** in toluene releases the 7,8-disubstituted bicyclo[4.2.1]nona-2,4,7-trienes **3** and $[(\eta^6\text{-}C_6H_5Me)Cr(CO)_3]$. Irradiation of solutions of **1** and dimethyl acetylenedicarboxylate at 0 °C yields the bicyclotriene as the major product but no organometallic complex. The diphenyl derivative **2a** undergoes a reversible intramolecular metal migration to the η^6-aryl species **4**. Irradiation of the azepine complex $[(\eta^6\text{-}C_6H_6N\{CO_2Et\})Cr(CO)_3]$ (**5**) and $R'C\equiv CR'$ (R' = Ph, $SiMe_3$) in toluene also forms [6 + 2] cycloadducts $[(\eta^{2:4}\text{-}C_8H_6N\{CO_2Et\}R'_2)Cr(CO)_3]$ (**6**). The heterobicyclotrienes **7** are isolated from **6** by treatment with iodine (R' = $SiMe_3$) or by heating in toluene (R' = Ph). X-ray crystal structures are reported for **6b** (R' = $SiMe_3$) [orthorhombic, $P2_12_12_1$, $a = 8.871(1)$, $b = 10.148(1)$, and $c = 26.017(4)$ Å, $R = 0.041$ for 2500 independent reflections] and a byproduct (**8**) that results from the endo [6 + 4] cycloaddition of *N*-carbethoxyazepine to **5**; monoclinic, $P2_1/c$, $a = 10.665(9)$, $b = 14.976(7)$, and $c = 13.004(7)$ Å, $\beta = 100.05(7)°$, $R = 0.047$ for 1044 independent reflections. Heating cycloheptatriene and alkynes $R'C\equiv CR'$ (R' = $SiMe_3$, Me, Et) in dibutyl ether with a catalytic amount of $Cr(CO)_6$ or $Fe_2(CO)_9$ also gives good yields of the [6 + 2] cycloadducts **3**, whereas the thermal reaction with dimethyl acetylenedicarboxylate in the presence of $Cr(CO)_6$ gives the known norcaradiene [4 + 2] adduct **9**.

Introduction

Transition-metal-mediated higher order cycloaddition reactions of trienes ([6 + 2] and [6 + 4]) are currently viewed as potentially powerful methodologies for the construction of medium size carbo- and heterocyclic rings.[1] The reactions were first reported by Pettit et al.[2] for iron species and later by Kreiter using chromium.[3] In addition, other isolated examples have appeared in the literature over the years.[4] More recently, Rigby has elegantly applied these and other new metal-promoted cycloadditions to a variety of synthetic problems.[1,5] The inherent advantages of using a metal complex to effect higher order cycloadditions are 2-fold: first, metal coordination of a triene, for example, usually favors the higher order process over competing [4 + 2] pathways; second, high facial selectivity is attained because the trienophile and triene are held within the metal coordination sphere prior to bond formation.

In an earlier report we presented preliminary results of the photoinduced [6 + 2] cycloaddition of alkynes to tricarbonyl(cycloheptatriene)chromium(0) (**1**), which ultimately gave bicyclo[4.2.1]nona-2,4,7-trienes.[6] This new reaction showed much promise over earlier titanium-catalyzed processes,[4b] in that a wider range of substrates could be employed without significant cyclotrimerization of the trienophile. In continuing our studies on the photoreactions of polyene complexes and alkynes,[7] we now present complete details of the [6 + 2] cycloaddition of alkynes to **1**, as well as the new [6 + 2] addition of alkynes and tricarbonyl(*N*-carbethoxyazepine)chromium(0), which leads to heterobicyclononatrienes. We also disclose full details of the metal-catalyzed thermally induced [6 + 2] cycloaddition of alkynes to cycloheptatriene, which proceeds with little or no cyclotrimerization of the alkyne substrates.

Results and Discussion

6 + 2 Cycloadditions of Alkynes to Tricarbonyl(η^6-cycloheptatriene)chromium(0). Irradiation of toluene or *n*-hexane solutions of tricarbonyl(η^6-cycloheptatriene)chromium(0) (**1a**) and $R'C\equiv CR'$ (R' = Ph, Tol, $SiMe_3$, Et) with UV light

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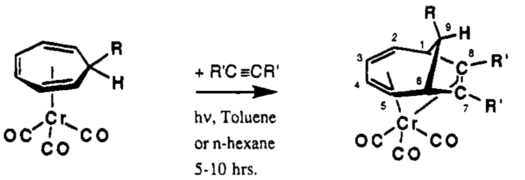
Table 1. ^1H and ^{13}C NMR Data for Complexes 1b,c, 2a–f, and 4[a,b]

complex	δ(^1H)	δ($^{13}C\{^1H\}$)
1b	4.01 (2H, t, $H_{1,6}$), 4.36 (1H, t, H_7), 4.97 (2H, m, $H_{2,5}$), 5.96 (2H, m, $H_{3,4}$), 6.75 (2H, m, Ph), 7.20 (3H, m, Ph)	
1c	1.86 (1H, d, H_7), 3.64 (6H, s, Me), 3.6–3.8 (3H, m, $H_{1,6,8}$), 4.84 (2H, m, $H_{2,5}$), 5.98 (2H, m, $H_{3,4}$)	35 (C_7), 52.6 (Me), 58.6 (C_8), 61.9 ($C_{1,6}$), 97.6 ($C_{3,4}$), 99.2 ($C_{2,5}$), 166.3 (*C*O$_2$Me), 231 (*C*O)
2a	0.91 (1H, d, $J_{H_{9'}H_9}$ = 11.9 Hz, $H_{9'}$), 1.74 (1H, m, H_9), 3.93 (2H, t, $J_{H_1H_9}$, $J_{H_6H_9}$ = 6.7 Hz, $J_{H_2H_1}$, $J_{H_5H_6}$ = 6.7 Hz, $H_{1,6}$), 4.42 (2H, m, $H_{2,5}$), 5.20 (2H, 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 (6H, m, Ph), 7.59 (4H, m, Ph)	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)
2b	0.88 (1H, d, $J_{H_{9'}H_9}$ = 11.6 Hz, $H_{9'}$), 1.69 (1H, q, $J_{H_9H_{9'}}$ = 11.6 Hz, $J_{H_9,H_{1,6}}$ = 5.2 Hz, H_9), 2.33 (6H, s, C*H*$_3$), 3.86 (2H, t, $J_{H_1H_9}$, $J_{H_6H_9}$ = 7.0 Hz, $J_{H_2H_1}$, $J_{H_5H_6}$ = 7.0 Hz, $H_{1,6}$), 4.37 (2H, m(brd), $H_{2,5}$), 5.17 (2H, 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 (4H, d, *J* = 8.0 Hz, C_6*H*$_4$Me), 7.45 (4H, d, *J* = 8.0 Hz, C_6*H*$_4$Me)	21.2 (C_6H_4*Me*), 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*$_6$H$_4$Me), 228, 232, 233 (CO)
2d	0.68 (1H, d, $J_{H_{9'}H_9}$ = 11.9 Hz, $H_{9'}$), 1.01 (6H, t, CH$_2$*Me*), 1.41 (1H, m, H_9), 2.26 (2H, m, C*H*$_2$), 2.48 (2H, m, C*H*$_2$), 3.29 (2H, t, $H_{1,6}$), 3.86 (2H, m, $H_{2,5}$), 5.00 (2H, m, $H_{3,4}$)	13.5 (*C*H$_3$), 22.0 (*C*H$_2$), 34.5 (C_9), 41.6 ($C_{1,6}$), 67.0 ($C_{2,5}$), 85.7 ($C_{7,8}$), 95.0 ($C_{3,4}$), 212, 230, 230.5 (CO)
2e	0.42 (18H, s, Si*Me*$_3$), 2.91 (1H, t, H_9), 3.32 (2H, dt, $H_{2,5}$), 3.90 (2H, dd, $H_{1,6}$), 4.76 (2H, m, $H_{3,4}$), 6.9–7.2 (5H, m, Ph)	1.4 (Si*Me*$_3$), 47.4 ($C_{1,6}$), 49.2 (C_9), 61.3 ($C_{2,5}$), 74.8 ($C_{7,8}$), 94.4 ($C_{3,4}$), 125.9, 128.1, 128.5, 136.3 (Ph), 229.6 (*C*O)
2f	0.35 (18H, s, Si*Me*$_3$), 2.11 (1H, s brd, H_9), 3.14 (2H, m brd, $H_{1,6}$), 3.26 (1H, d, H_{10}), 3.40 (2H, m brd, $H_{2,5}$), 3.69 (6H, s, CO$_2$*Me*), 5.00 (2H, m brd, $H_{3,4}$)	1.3 (Si*Me*$_3$), 43.5 (C_9), 46.9 ($C_{1,6}$), 47.2 (C_{10}), 52.6 (CO$_2$*Me*), 60.3 ($C_{2,5}$), 73.8 ($C_{7,8}$), 93.4 ($C_{3,4}$), 168.7 (*C*O$_2$Me), 229.3 (*C*O)
4	1.77 (1H, d, $J_{H_{9'}H_9}$ = 11.5 Hz, $H_{9'}$), 2.60 (1H, m, H_9), 3.51 (1H, t, H_1), 3.68 (1H, t, H_6), 5.03 (2H, s brd, Ph), 5.28 (2H, m, Ph), 5.45 (1H, d, Ph), 5.90 (3H, m, $H_{3,4,5}$), 6.35 (1H, m, H_2), 7.20 (5H, s, brd, Ph)	30.1 (C_9), 48.7, 49.2 (C_1,C_6), 90.7, 91.2, 91.4, 93.5, 94.8, 106.2 (*Ph*-Cr), 124.4, 124.8 (C_2, C_5), 127.3, 127.6, 128.1 (*Ph*), 131.8, 135.1 ($C_{7,8}$), 138.0, 138.6 ($C_{3,4}$), 139.6 (*Ph*), 233 (CO)

[a] Assignments refer to eq 1. [b] In $CDCl_3$.

results in neutral bicyclo[4.2.1]nona-2,4,7-triene complexes [($\eta^{4:2}$-$C_9H_7R'_2$)Cr(CO)$_3$] (**2a**–**d**, eq 1). These species form via cycloaddition of the alkynes to the 1 and 6 carbons of the cycloheptatriene ring. The new bicyclic ligand acts as a chelate through η^4-coordination to C(2)–C(5) and η^2-bonding to C(7)–C(8).



(1)

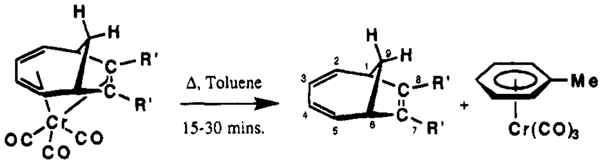
1a R = H.
1b R = Ph.
1c R = CH(CO$_2$Me)$_2$.

2a R = H, R' = Ph, 85%.
2b R = H, R' = Tol, 86%.
2c R = H, R' = SiMe$_3$, 80%.
2d R = H, R' = Et, 29%.
2e R = Ph, R' = SiMe$_3$, 94%.
2f R = CH(CO$_2$Me)$_2$, R' = SiMe$_3$, 50%.

Complexes **2a**–**f** were isolated as analytically pure deep red crystalline solids in near-quantitative yield (**2a**–**c**,**e**) and characterized using IR, ^1H NMR, and ^{13}C NMR spectroscopy (Table 1). Complex **2d** was similarly characterized but could only be isolated in 29% yield due to facile decomplexation of the ligand (detected by GCMS). Optimum yields of **2d** were obtained when the reaction solution was purged with CO prior to photolysis. The proton and ^{13}C NMR data for **2a**–**f** are consistent with the assigned structures, and signal assignments were made by comparison with published data for **2c**.[4a]

The substituted complexes [(η^6-C_7H_7R)Cr(CO)$_3$] (**1b**, R = Ph; **1c**, R = CH{CO$_2$Me}$_2$), prepared by addition of the appropriate carbanion to [(η^6-C_7H_7)Cr(CO)$_3$][PF$_6$], also add bis(trimethylsilyl)acetylene under photochemical conditions to give the bicyclononatriene complexes **2e**,**f** bearing an exo substituent at C(9) (eq 1). These latter products serve to show that the reactions can be conducted when there are substitutents at C(7) of **1** and, more importantly, that the addition is selective to the endo face of the coordinated triene. The ^1H NMR signal for H(9) in **2e**,**f** has a similar chemical shift to that assigned as H(9) in **2c** and is consistent with addition to the face of the ring opposite the phenyl or CH(CO$_2$Me)$_2$ substituents.

The bicyclo[4.2.1]nona-2,4,7-trienes can be decomplexed from the metal by heating toluene solutions of **2** for 15–30 min. The deep red solutions quickly turn yellow due to formation of tricarbonyl(η^6-toluene)chromium(0), and the pure organic compounds were isolated (TLC, silica) as white crystalline solids or colorless oils and spectroscopically characterized (eq 2; Table 2). Complex **2c** does not yield the triene when heated in toluene nor when treated with iodine; however, oxidative decomplexation of the ligand with Ce^{IV} has been previously reported by Grevels et al.[4a]

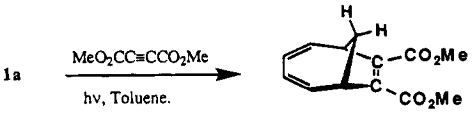


(2)

2a R' = Ph.
2b R' = Tol.
2d R' = Et.

3a,b,d
29-38%

In contrast, irradiation of solutions of **1a** and dimethyl acetylenedicarboxylate (DMAD, MeO$_2$CC≡CCO$_2$Me) with UV light gives 7,8-bis(carbomethoxy)bicyclo[4.2.1]nona-2,4,7-triene (**3g**) directly in 66% isolated yield, (eq 3). A slight excess of alkyne is ideal, but a large excess leads to some arene, C_6(CO$_2$Me)$_6$, via cyclotrimerization of DMAD, as well as traces of the [4 + 2] cycloadducts of **3g** and DMAD. These latter products were identified by GCMS, whereas **3g** was characterized from its ^1H and ^{13}C NMR and mass spectroscopic data which are similar to those of **3a**–**d**.



(3)

3g 66%

The stability of complexes **2a**–**d** toward substitution of the bicyclic ligand is highly dependent upon the groups attached to C(7) and C(8). Thus, complex **2c** (R′ = SiMe$_3$) is very stable and requires a strong oxidant (Ce^{IV})[4a] to remove the organic

Table 2. ^{1}H and ^{13}C NMR Data for 7,8-Disubstituted Bicyclo[4.2.1]nona-2,4,7-dienes 3 and 9[a,b]

complex	$\delta(^1H)$	$\delta(^{13}C)$
3b, R′ = Tol	1.81 (1H, d, $J_{H_{9'}H_9}$ = 11 Hz, $H_{9'}$), 2.31 (6H, s, $C\mathit{H}_3$), 2.58 (1H, m, $J_{H_9H_{9'}}$ = 11 Hz, $J_{H_9H_{1,6}}$ = 7 Hz, H_9), 3.62 (2H, 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 (2H, dt, $H_{2,5}$), 6.28 (2H, m, $H_{3,4}$), 6.98 (4H, d, J = 8.0 Hz, $C_6\mathit{H}_4Me$), 7.09 (4H, d, J = 8.0 Hz, $C_6\mathit{H}_4Me$)	21.1 ($C_6H_4\mathit{Me}$), 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)
3d, R′ = Et	0.98 (6H, t, J = 7.8 Hz, $C\mathit{H}_3CH_2$), 1.53 (1H, d, J = 11 Hz, $H_{9'}$), 2.03 (2H, m, $C\mathit{H}_2Me$), 2.10 (2H, m, $C\mathit{H}_2Me$), 2.61 (1H, m, H_9), 3.08 (2H, t, J = 7.6 Hz, $H_{1,6}$), 5.70 (2H, dt, $H_{2,5}$), 6.15 (2H, m, $H_{3,4}$)	14.4 ($CH_2\mathit{Me}$), 19.1 ($\mathit{C}H_2Me$), 30.9 (C_9), 46.0 (C_1,C_6), 123.6 (C_2, C_5), 136.1 (C_7,C_8), 140.5 (C_3,C_4)
3g, R′ = CO_2Me	1.61 (1H, d, $J_{H_{9'}H_9}$ = 12 Hz, $H_{9'}$), 2.33 (1H, m, H_9), 3.56 (2H, t, $J_{H_1H_2}$, $J_{H_6H_5}$ = 7 Hz, $J_{H_1H_9}$, $J_{H_6H_9}$ = 7 Hz, $H_{1,6}$), 3.76 (6H, s, Me), 5.97 (2H, m, $H_{2,5}$), 6.17 (2H, m, $H_{3,4}$)	29.8 (C_9), 45.0 (Me), 52.3 (C_1,C_6), 126.0 (C_2, C_5), 132.7 (C_7,C_8), 136.8 (C_3,C_4), 165.3 ($\mathit{C}O_2Me$)
3h, R′ = Me	1.38 (1H, d, J = 11 Hz, $H_{9'}$), 1.50 (6H, s, $C\mathit{H}_3$), 2.04 (1H, m, H_9), 2.81 (2H, t, J = 7.0 Hz, $H_{1,6}$), 5.60 (2H, dd, $H_{2,5}$), 6.06 (2H, m, $H_{3,4}$)	11.1 (*Me*), 30.4 (C_9), 48.6 (C_1,C_6), 123.9 (C_2,C_5), 131.0 (C_7,C_8), 140.9 (C_3,C_4)
9	0.62 (1H, m, $H_{3'}$), 0.73 (1H, m, H_3), 1.40 (2H, m, $H_{2,4}$), 3.70 (6H, s, CH_3), 4.07 (2H, m, $H_{2,5}$), 6.04 (2H, m, $H_{8,9}$)	16.9 (C_3), 17.8 ($C_{2,4}$), 40.8 ($C_{1,5}$), 52.1 ($O\mathit{C}H_3$), 130.0 ($C_{8,9}$), 148.0 ($C_{6,7}$), 167 (s, *C*O)

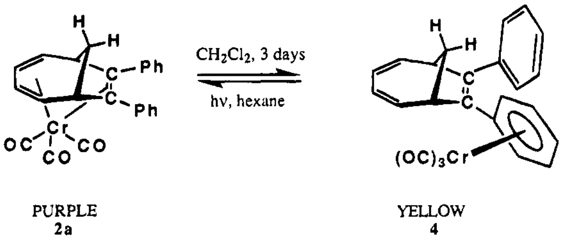
[a] Assignments refer to eqs 2 and 8. [b] In $CDCl_3$.

Table 3. ^{1}H and ^{13}C NMR Data for Complexes 6, 7, and 8[a,b]

complex	$\delta(^1H)$	$\delta(^{13}C)$
6a	1.28 (3H, t, $CH_2\mathit{Me}$), 4.17 (2H, q, $C\mathit{H}_2Me$), 4.62 (2H, m, $H_{2,5}$), 5.24 (2H, m, $H_{3,4}$), 5.40 (1H, d, H_1 or H_6), 5.61 (1H, H_1 or H_6), 7.3 (6H, m, Ph), 7.60 (4H, d, Ph)	14.4 ($CH_2\mathit{Me}$), 61.6 ($\mathit{C}H_2Me$), 62.2, 63.0 ($C_{1,6}$), 71.0, 71.4 ($C_{2,5}$), 86.4, 88.0 ($C_{7,8}$), 94.1, 94.6 ($C_{3,4}$), 128.0, 129.0, 130.0, 130.2, 131.0, 131.6 (Ph), 151.8 ($\mathit{C}O_2Et$), 227.0, 227.6, 231.6 (CO)
6b	0.40 (9H, s, $Si\mathit{Me}_3$), 0.41 (9H, s, $Si\mathit{Me}_3$), 1.21 (3H, t, $CH_2\mathit{Me}$), 3.73 (2H, m, $H_{2,5}$), 4.05 (2H, q, $C\mathit{H}_2Me$), 4.9 (3H, m, $H_{3,4}$ and H_1 or H_6), 5.09 (1H, d, H_1 or H_6)	1.0 ($Si\mathit{Me}_3$), 14.3 ($CH_2\mathit{Me}$), 61.9 ($\mathit{C}H_2Me$), 62.4 ($C_{1,6}$), 67.0 ($C_{2,5}$), 73.4, 74.1 ($C_{7,8}$), 90.8, 91.2 ($C_{3,4}$), 151.2 ($\mathit{C}O_2Et$), 229.2 (CO)
7a	1.25 (3H, t, $CH_2\mathit{Me}$), 4.16 (2H, q, $C\mathit{H}_2Me$), 5.31 (1H, d, H_1 or H_6), 5.42 (1H, d, H_1 or H_6), 5.98 (2H, m, $H_{2,5}$), 6.38 (2H, m, $H_{3,4}$), 7.20 (10H, m, Ph)	14.2 ($CH_2\mathit{Me}$), 60.4 ($\mathit{C}H_2Me$), 64.2 ($C_{1,6}$), 124.4 ($C_{2,5}$), 126.0 ($C_{7,8}$), 126.8, 127.2, 127.6, 130.6 (Ph), 138.8 ($C_{3,4}$), 153.5 ($\mathit{C}O_2Et$)
7b	0.18 (18H, s, $Si\mathit{Me}_3$), 1.17 (3H, t, $CH_2\mathit{Me}$), 4.04 (2H, q, $C\mathit{H}_2Me$), 4.91 (1H, d, H_1 or H_6), 5.00 (1H, d, H_1 or H_6), 5.87 (2H, m, $H_{2,5}$), 6.20 (2H, m, $H_{3,4}$)	1.3 ($Si\mathit{Me}_3$), 14.7 ($CH_2\mathit{Me}$), 60.8 ($\mathit{C}H_2Me$), 66.8, 67.2 ($C_{1,6}$), 124 ($C_{2,5}$), 124.5 ($C_{7,8}$), 137.2 ($C_{3,4}$), 153.4 ($\mathit{C}O_2Et$)
8	1.12 (3H, t, *Me*), 1.25 (3H, t brd, *Me*), 3.8 (1H, m), 3.95 (2H, m), 4.2 (2H, m brd), 4.55 (1H, m), 4.68 (1H, m brd), 4.84 (1H, t), 4.98 (1H, t), 5.06 (1H, m), 5.12 (1H, m), 5.29 (1H, s brd), 5.42 (1H, m), 5.8 (1H, d brd), 6.26 (1H, m), 6.86 (1H, d brd)	14.4, 14.6, 48.5, 48.8, 58.6, 60.3, 62.3, 62.6, 63.3, 63.5, 88.5, 91.9, 92.4, 99.7, 115.2, 115.6, 155.2, 155.4, 230.8, 232.2, 234.9

[a] Assignments refer to eqs 5 and 6. [b] In $CDCl_3$.

species, whereas the aryl derivatives are moderately stable and decomplex in toluene. In contrast, **2d** requires a CO atmosphere, during the reaction between **1** and 3-hexyne, to prevent decomplexation and ultimately forms a mixture of organic and organometallic products. On the other hand, the bis(carbomethoxy) complex cannot be detected, even with a CO purge of the reaction solution. The lability of the bicyclic complexes is further exemplified by a rearrangement of the diphenyl species **2a**. Thus, if CH_2Cl_2 solutions of **2a** are stirred over 3 days, the red-purple color slowly disappears and a yellow solution results. The resulting product shows a complex ^{1}H NMR spectrum consistent with an asymmetric bicyclic ring and one aryl group bonded to chromium (eq 4). The product **4** results from an intramolecular migration of the metal from the bicyclic ring to a pendant aryl group at C(7) and suggests the η^6-aryl species is the most thermodynamically stable isomer in dichloromethane. Surprisingly, the migration can be reversed in 39% yield via photolysis of **4** in hexane. This latter transformation may proceed because **2a** is more symmetric and less polar than **4** and consequently favored in *n*-hexane solution. Alternatively, **2a** and **4** may readily interchange under photochemical conditions, but **2a** precipitates from a *n*-hexane solution.

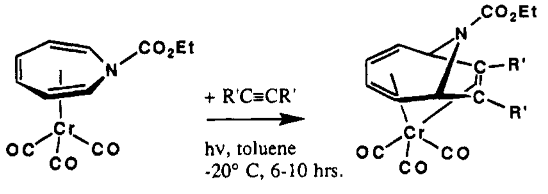


(4)

PURPLE
2a

YELLOW
4

6 + 2 Cycloadditions of Alkynes to Tricarbonyl{η^6-*N*-carbethoxyazepine}chromium(0). Irradiation of toluene or *n*-hexane solutions of tricarbonyl{η^6-*N*-carbethoxyazepine}-chromium(0)[8] (**5**) and R′C≡CR′ (R′ = Ph, $SiMe_3$) gives the disubstituted 9-azabicyclo[4.2.1]nona-2,4,7-triene complexes {$\eta^{4:2}$-$C_8(NCO_2Et)H_6R'_2$}$Cr(CO)_3$ (**6a,b**) (eq 5). As is the case for **2**, complexes **6a,b** arise from a [6 + 2] cycloaddition, in this case between an alkyne and the 1 and 6 carbons of the *N*-carbethoxyazepine ring.



(5)

5

6a R = Ph, 68%.
6b R = $SiMe_3$, 63%.

The new bicyclic complexes **6a,b** were isolated as analytically pure deep red crystalline solids in moderate yields and spectroscopically characterized (Table 3). The NMR spectral data

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[8] Kreiter, C. G.; Özkar, S. *Z. Naturforsch.* **1977**, *32B*, 408.

Table 4. Crystal Data for Compounds 6b and 8

	6b	**8**
formula	$C_{20}H_{29}CrNO_5Si_2$	$C_{21}H_{22}CrN_2O_7$
fw	471.6	466.4
space group	$P2_12_12_1$	$P2_1/c$
a, Å	8.871(1)	10.665(9)
b, Å	10.148(1)	14.976(7)
c, Å	26.017(4)	13.004(7)
β, deg	N/A	100.05(7)
V, Å^3	2342.1(6)	2045(2)
Z	4	4
D(calc), g cm^{-3}	1.338	1.515
μ(Mo Kα), cm^{-1}	62	60.7
radiation	Mo Kα(λ = 0.71073 Å)	
$R(F)$, %[a]	4.1	4.69
$R_w(F)$, %[a]	5.2	4.72

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w(F) = \sum(w^{1/2}(|F_o| - |F_c|))/w^{1/2}(|F_o|)$.

Table 5. Selected Bond Distances and Angles for 6b

	(a) Bond Distances (Å)		
Cr−C(2)	2.330(4)	Cr−C(3)	2.201(4)
Cr−C(4)	2.195(4)	Cr−C(5)	2.376(4)
Cr−C(7)	2.471(4)	Cr−C(8)	2.440(4)
Cr−C(12)	1.833(5)	Cr−C(13)	1.824(5)
Cr−C(14)	1.846(5)	Si(1)−C(8)	1.902(4)
Si(2)−C(7)	1.886(4)	O(2)−C(9)	1.221(6)
O(3)−C(12)	1.170(7)	O(4)−C(13)	1.160(6)
O(5)−C(14)	1.159(7)	N−C(1)	1.449(5)
N−C(9)	1.343(5)	N−C(6)	1.445(5)
C(1)−C(2)	1.525(6)	C(1)−C(8)	1.533(6)
C(2)−C(3)	1.370(6)	C(3)−C(4)	1.450(7)
C(4)−C(5)	1.357(7)	C(5)−C(6)	1.513(6)
C(6)−C(7)	1.547(6)	C(7)−C(8)	1.372(6)
	(b) Bond Angles (deg)		
C(2)−Cr−C(14)	167.3(2)	C(3)−Cr−C(14)	153.0(2)
C(4)−Cr−C(12)	145.6(2)	C(5)−Cr−C(12)	168.3(2)
C(7)−Cr−C(13)	160.1(2)	C(8)−Cr−C(13)	167.5(2)
N−C(1)−C(2)	111.0(3)	C(1)−N−C(6)	108.8(3)
N−C(1)−C(8)	102.8(3)	C(6)−N−C(9)	128.1(4)
N−C(6)−C(5)	112.2(4)	N−C(6)−C(7)	103.2(3)
C(2)−C(1)−C(8)	105.5(3)	C(1)−C(2)−C(3)	125.6(4)
C(2)−C(3)−C(4)	126.4(4)	C(3)−C(4)−C(5)	127.9(4)
C(4)−C(5)−C(6)	125.5(4)	C(5)−C(6)−C(7)	104.3(3)
C(6)−C(7)−C(8)	107.8(3)	C(1)−C(8)−C(7)	109.4(3)
Cr−C(7)−Si(2)	122.4(2)	Cr−C(8)−Si(1)	118.9(2)
O(2)−C(9)−N	123.8(4)	Cr−C(12)−O(3)	172.9(4)
Cr−C(13)−O(4)	176.9(5)	Cr−C(14)−O(5)	173.7(4)

for **6a,b** show some asymmetry in the bicyclic ring that is not observed for the carbocyclic analogs. Thus, the ^{1}H NMR spectrum of **6a** shows two doublets for H(1) and H(6) at δ 5.4 and 5.6, and the ^{13}C NMR spectrum shows eight unique signals for carbons 1 through 8 of the heterobicyclic ring. Complex **6b** was also characterized by an X-ray diffraction study (Tables 4 and 5 and Figure 1). The complex is essentially octahedral at chromium with the three-coordinated double bonds trans to carbonyl ligands. The C(7)=C(8) bond is noticeably further (av 2.456 Å) from the metal than the coordinated diene C(2)−C(5) (av 2.276 Å). The structure shows that the observed asymmetry of the ring derives from the orientation of the carbethoxy substituent at nitrogen such that the ethoxy and carbonyl groups are above C(6) and C(1), respectively. In order for two distinct signals to be observed for H(1) and H(6), there must be restricted rotation about the N−C(9) bond. This is confirmed by the partial double-bond character of N−C(9) (1.343 Å) compared to C(1)−N and C(6)−N (av 1.447 Å).

The 9-azabicyclo[4.2.1]nona-2,4,7-triene ligands can also be readily decomplexed from the metal. Thus, if a toluene solution of **6a** is refluxed for 5 min, a ligand exchange occurs forming **7a** and tricarbonyl(η^6-toluene)chromium(0). Complex **6b** is more robust, and oxidative decomplexation with iodine is required to release the organic **7b**. In general **6a,b** are less stable to air and heat than the carbocyclic species **2**. The pure organic compounds **7a,b** were isolated (TLC, silica) as colorless oils and characterized by NMR spectroscopy and high-resolution mass spectroscopy (eq 6; Table 3). Compounds **7a,b** show no unusual features in either their ^{1}H NMR or ^{13}C NMR spectra but do possess the asymmetry associated with the *N*-carbethoxy group.

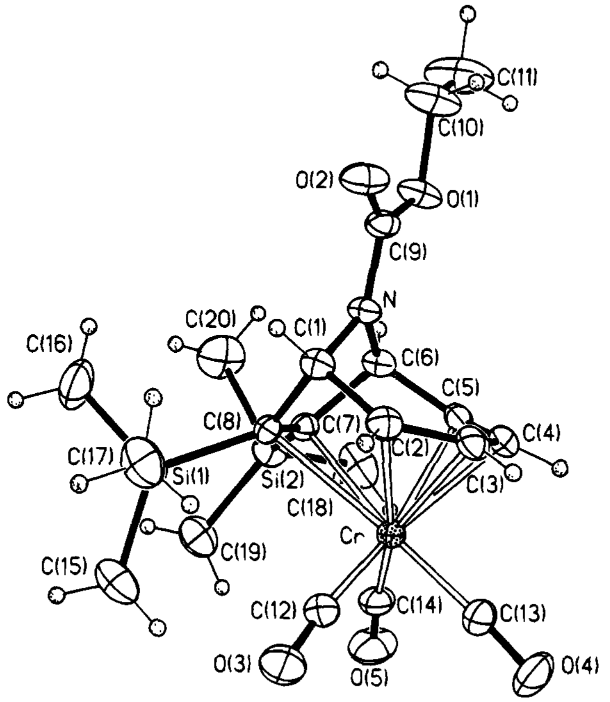
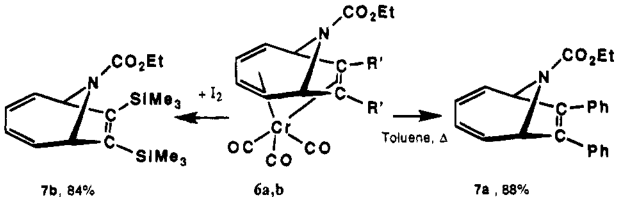


Figure 1. Molecular structure and labeling scheme for **6b**.



(6)

If the azepine complex **5** is not purified immediately prior to the reaction with alkynes, an organometallic byproduct (**8**) is formed in low yield. This species was isolated as an orange crystalline solid and characterized using IR and NMR spectroscopy as well as by an X-ray crystallography study (Tables 3, 4, and 6 and Figure 2). The complex contains a tricyclic ligand that is an endo [6 + 4] cycloaddition dimer of *N*-carbethoxyazepine coordinated to a $Cr(CO)_3$ group. The structure is similar to that of **6b** with an octahedral coordination sphere consisting of three carbonyl ligands trans to the double bonds of the tricyclic ligand. Most features of the structure are identical to those of **6b** (e.g., the $N-CO_2Et$ bonds are relatively short {N(1)−C(13) 1.368(11) Å}).

Complex **8** can form in one of two ways: (i) via a [6 + 4] cycloaddition of *N*-carbethoxyazepine to **5**; (ii) through the thermal dimerization of azepine followed by coordination to chromium. We believe **8** is formed via route (i) because it is isolated from reactions performed at −20 °C, whereas the thermal dimerization of azepines has been reported to occur at 130 °C.[9] Moreover, the thermal dimers are exo adducts and the ligand in **8** is an endo dimer. The endo product would be

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[9] Paquette, L. A.; Barrett, J. A.; Kuhla, D. E. *J. Am. Chem. Soc.* **1969**, *91*, 3616.

Table 6. Selected Bond Distances and Angles for 8

(a) Bond Distances (Å)			
Cr−C(2)	2.255(10)	Cr−C(3)	2.191(11)
Cr−C(4)	2.188(10)	Cr−C(5)	2.291(9)
Cr−C(8)	2.440(9)	Cr−C(9)	2.422(9)
Cr−C(19)	1.868(12)	Cr−C(20)	1.863(12)
Cr−C(21)	1.820(11)	O(1)−C(13)	1.217(14)
O(2)−C(13)	1.348(14)	O(2)−C(14)	1.448(12)
O(3)−C(16)	1.207(15)	O(4)−C(16)	1.347(13)
O(4)−C(17)	1.449(12)	O(5)−C(19)	1.122(14)
O(6)−C(20)	1.146(14)	O(7)−C(21)	1.163(13)
N(1)−C(1)	1.471(13)	N(1)−C(6)	1.459(12)
N(1)−C(13)	1.369(13)	N(2)−C(7)	1.455(12)
N(2)−C(11)	1.387(13)	N(2)−C(16)	1.377(14)
C(1)−C(2)	1.528(14)	C(1)−C(10)	1.533(15)
C(2)−C(3)	1.375(16)	C(3)−C(4)	1.453(14)
C(4)−C(5)	1.393(13)	C(5)−C(6)	1.500(12)
C(6)−C(7)	1.526(14)	C(7)−C(8)	1.544(14)
C(8)−C(9)	1.332(14)	C(9)−C(10)	1.522(14)
C(10)−C(12)	1.486(13)	C(11)−C(12)	1.394(14)

(b) Bond Angles (deg)			
C(2)−Cr−C(19)	171.7(4)	C(3)−Cr−C(19)	147.1(5)
C(4)−Cr−C(20)	143.3(4)	C(5)−Cr−C(20)	163.6(4)
C(19)−Cr−C(20)	98.2(5)	C(8)−Cr−C(21)	155.6(4)
C(19)−Cr−C(21)	79.0(5)	C(20)−Cr−C(21)	81.4(5)
C(9)−Cr−C(21)	155.0(4)	C(1)−N(1)−C(6)	121.9(7)
C(1)−N(1)−C(13)	115.4(8)	C(7)−N(2)−C(11)	125.2(8)
C(11)−N(2)−C(16)	119.7(8)	N(1)−C(1)−C(2)	113.0(8)
N(1)−C(1)−C(10)	111.4(8)	C(2)−C(1)−C(10)	108.3(8)
C(1)−C(2)−C(3)	129.9(9)	C(2)−C(3)−C(4)	122.8(9)
C(3)−C(4)−C(5)	122.6(9)	C(4)−C(5)−C(6)	129.4(9)
C(5)−C(6)−C(7)	107.0(7)	N(1)−C(6)−C(5)	115.0(7)
N(1)−C(6)−C(7)	112.6(8)	N(2)−C(7)−C(6)	112.9(7)
N(2)−C(7)−C(8)	113.4(8)	C(6)−C(7)−C(8)	110.9(7)
C(7)−C(8)−C(9)	121.8(9)	C(8)−C(9)−C(10)	122.1(9)
C(1)−C(10)−C(9)	113.0(8)	C(1)−C(10)−C(12)	115.3(8)
C(9)−C(10)−C(12)	109.3(8)	N(2)−C(11)−C(12)	126.9(9)
C(10)−C(12)−C(11)	126.0(9)	O(2)−C(13)−N(1)	111.8(9)
O(4)−C(16)−N(2)	112.1(10)	Cr−C(20)−O(6)	177.0(9)
Cr−C(19)−O(5)	175.2(9)	Cr−C(21)−O(7)	175.3(10)

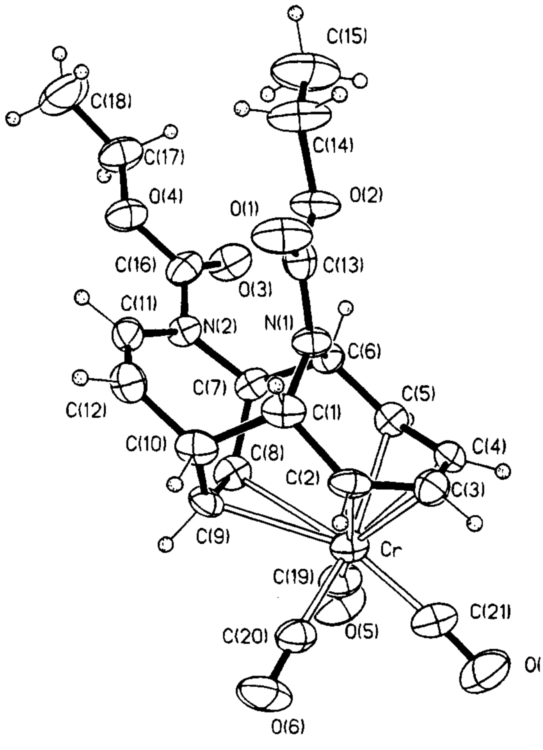
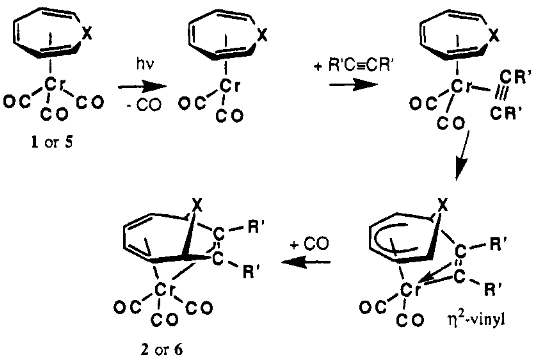


Figure 2. Molecular structure and labeling scheme for **8**.

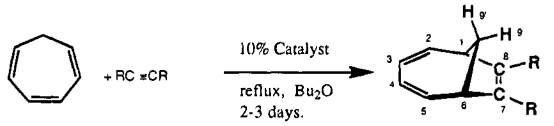
that expected from a metal-promoted process. This type of [6 + 4] cycloaddition is similar to those reported by Rigby for **5** and dienes.[1,5] Complex **8** can be eliminated from the reactions by using an excess of alkyne and freshly prepared **5**. Therefore, no further studies on this species were performed.

Scheme 1. Proposed Mechanism for the Formation of **2** and **6**. X = CH_2 or NCO_2Et



Mechanism of the [6 + 2] Cycloadditions. Given the similarity in the structures of **1** and **5** and the observation that each leads to similar products, it is reasonable to assume that a common pathway exists in the formation of the adducts **2** and **6**. On the basis of the related [6 + 4] reaction of **1** with dienes[3,5a,g,10] and [6 + 2] addition to olefins,[5b] we believe our reactions proceed similarly via the proposed mechanism shown in Scheme 1. As shown, a vacant coordination site is photogenerated at the metal and an alkyne coordinates to this site prior to C−C bond formation. The absolute role of UV light in the [6 + 4] reaction has been the subject of some debate, but detailed studies by Stufkens[10] show that two primary photoprocesses exist for **1**, a photoinduced ring slip and photolytic CO loss. These authors concluded that carbonyl loss was the pathway responsible for the adducts, although Rigby and co-workers have suggested a ring slip mechanism based upon the efficiency of the reactions under a constant purge of argon.[1] They argued that the purge should reduce the yields if CO ejection and recapture is involved. However, it is possible that the recapture of CO occurs by abstraction of a carbonyl from a molecule of **1** or **5**, a process that would be relatively unaffected by a purge since it is potentially autocatalytic. Clearly, more studies are required to fully elucidate these novel processes; nonetheless, Scheme 1 shows what we believe to be the most likely routes to **2** and **6**.

Thermally Induced Catalytic 6 + 2 Cycloadditions of Alkynes to Cycloheptatriene. Rigby and co-workers have reported that the [6 + 2] and [6 + 4] cycloaddition reactions of **1** can be driven thermally in the presence of a metal catalyst.[1,5c] Similarly, the [6 + 2] reactions of alkynes and cycloheptatriene occur at elevated temperatures with 10% of a metal carbonyl complex present. Thus, if dibutyl ether solutions of cycloheptatriene, alkynes R′C≡CR′ (R′ = TMS, Et, Me), and 0.1 equiv of $Cr(CO)_6$ are refluxed for 2−3 days, the [6 + 2] adducts **3c,d,h** are formed (eq 7).



(7)

Catalyst = $Cr(CO)_6$ or $Fe_2(CO)_9$

3c R = TMS, 65%.
3d R = Et, 47%.
3h R = Me, 81%.

The bicyclononatrienes **3c,d,h** can readily be prepared in gram quantities via this route and are virtually pure following flash chromatography. All were characterized by comparison of their

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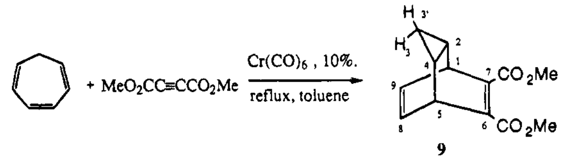
[10] van Houwelingen, T.; Stufkens, D. J.; Oskam, A. *Organometallics* **1992**, *11*, 1146.

spectroscopic data with those reported (**3c**)[4a] or by NMR and high-resolution mass spectroscopy (**3d,h**). Surprisingly, diphenylacetylene does not react with cycloheptatriene under these conditions, possibly because the catalyst can bond to the aryl group of this alkyne, forming (η-$C_6H_5\{C_2Ph\}$)$Cr(CO)_3$. The reactions absolutely require a catalyst since refluxing the alkynes with cycloheptatriene in dibutyl ether for 2 days without a metal species failed to give [6 + 2] cycloadducts. In addition to $Cr(CO)_6$, $Cr(CO)_3(\eta^6\text{-}C_7H_8)$ and $Fe_2(CO)_9$ are also good catalysts, with the optimal catalyst-to-substrate ratio being 1:10. The metal complexes are slightly air sensitive and partially decompose at lower ratios, whereas at very high ratios organometallic products are formed. Therefore, both higher and lower ratios reduce the yields of the organic products.

In contrast, when toluene solutions of cycloheptatriene are heated, 1 equiv of DMAD, and 0.1 equiv of $Cr(CO)_6$ gave *exo*-dimethyl tricyclo[3.2.2.0^{2,4}]nona-6,8-diene-6,7-dicarboxylate (**9**) in 40% yield, derived from a [4 + 2] cycloaddition of DMAD and norcaradiene (eq 8). Compound **9** was spectroscopically characterized (NMR, HRMS, Table 2) and is the known product that results from heating C_7H_8 and DMAD in toluene.[11] This observation is contrary to the results reported by Rigby with ethyl acrylate in which they observed no norcaradiene adducts when a metal catalyst was present.[5c] The different results for DMAD may be because it is a better dienophile than ethyl acrylate and the other alkynes used herein and is able to trap the norcaradiene form of cycloheptatriene. Reaction of DMAD and cycloheptatriene in Bu_2O also gives **9**, but in lower yields than in toluene.



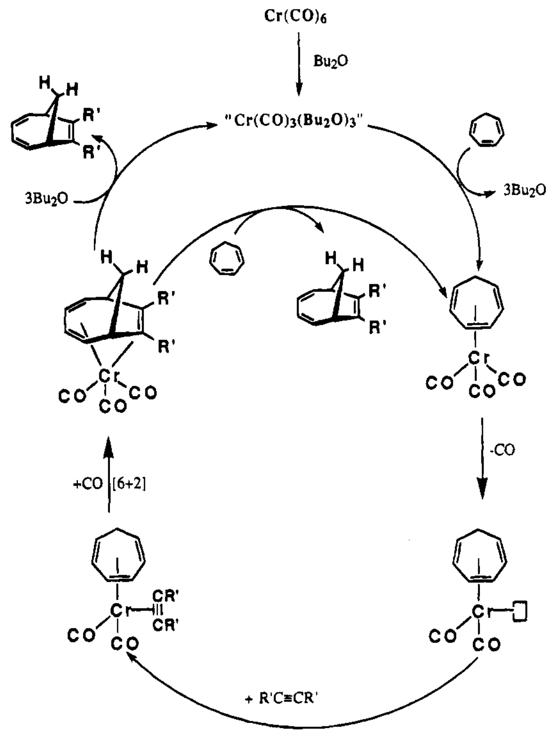
9 (8)

Mechanism of the Thermal Process. A plausible mechanism for the respective [6 + 2] and [6 + 4] catalytic cycloadditions of olefins and dienes to cycloheptatriene has been proposed.[5c] A modification, which we believe to be that followed by the alkyne additions, is shown in Scheme 2. As shown, initial thermolysis of $Cr(CO)_6$ in Bu_2O gives a possible precatalyst "$(Bu_2O)_3Cr(CO)_3$". Subsequent substitution of cycloheptatriene for Bu_2O gives [$Cr(CO)_3(\eta^6\text{-}C_7H_8)$], and dissociation of CO creates a vacant coordination site. Binding of the alkyne and insertion into the Cr−C(1) and Cr−C(6) bonds gives the coordinated cycloadduct which can re-form the catalytic species by displacement of the organic adduct directly with cycloheptatriene or indirectly with Bu_2O. We have observed that the reactions proceed, albeit in lower yield, without any solvent other than the alkyne or cycloheptatriene, indicating the Bu_2O complex is not absolutely necessary and that dibutyl ether may merely provide an elevated temperature for the reaction to proceed. Presumably $Fe_2(CO)_9$ acts as a catalyst through the formation of tricarbonyl(η^4-cycloheptatriene)iron(0), which is known to undergo a [6 + 2] cycloaddition with alkynes.[2]

Conclusions

Detailed studies of the [6 + 2] cycloaddition of alkynes to cycloheptatriene and *N*-carbethoxyazepine complexes have been presented in which substituted bicyclo[4.2.1]nona-2,4,7-trienes are generated. The reactions are either photoassisted and stoichiometric in metal complex or catalytic in metal but thermally driven. The extension of this new coupling reaction to other alkynes and the development of new metal-mediated cycloadditions which complement those described herein and in ref 1 are currently under investigation.

Scheme 2. Proposed Mechanism for the $Cr(CO)_6$-Catalyzed [6 + 2] Process



Experimental Section

General. The preparation, purification, and reactions of all complexes described were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Manipulations of air-sensitive solids were performed inside a Braun MB 150 inert atmosphere glove box containing a nitrogen atmosphere. Solvents were dried over Na/benzophenone (toluene, benzene, THF, diethyl ether), CaH_2 (*n*-hexane, *n*-pentane, CH_2Cl_2), or K_2CO_3 (acetone) and were freshly distilled prior to use. Reagents were used as supplied by Aldrich, Janssen Chimica, or Farchan. Infrared spectra were recorded on a Nicolet 5ZDX FT instrument operated in the transmittance mode, and all NMR spectra were recorded on a Varian VXR-400S NMR Fourier transform spectrometer. Gas chromatography−mass spectrometry (GCMS) was performed using a Hewlett−Packard HP5890 gas chromatograph connected to a Finnegan Mat Incos 50 mass spectrometer (70 eV). High-resolution mass spectra were obtained at Hoffman La Roche (Nutley, NJ). Microanalyses were carried out by Robertson Microlit Laboratories (Madison, NJ). Chromatography was performed on alumina (150 mesh, standard grade, activated, neutral, from Aldrich), silica gel (230−425 mesh), or Florosil (100−200 mesh, from Fisher Scientific). Tricarbonyl(η-cycloheptatrienyl)chromium(0) hexafluorophosphate[12] and tricarbonyl(η^6-*N*-carbethoxyazepine)chromium(0)[8] were prepared using the literature procedures. Photolyses were conducted in Pyrex or quartz flasks (fitted with a cooling jacket if necessary) and placed approximately 5 cm from a water-cooled quartz well containing a 450 W Hanovia medium pressure Hg lamp.

Tricarbonyl(7-*exo*-phenylcycloheptatriene)chromium(0) (1b). Phenylmagnesium bromide (0.85 mL of a 3.0 M solution in THF, 2.55 mmol) was added to a vigorously stirred suspension of tricarbonyl(η-cycloheptatrienyl)chromium hexafluorophosphate (0.73 g, 1.96 mmol) in THF (50 mL) at −78 °C. The mixture was allowed to warm to room temperature over 1 h and was filtered through alumina (2 × 3 cm), and the solvent was removed in vacuo. The residue was

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(11) Goldstein, M. J.; Gevirtz, A. H. *Tetrahedron Lett.* **1965**, *49*, 4413.

(12) Munro, J. D.; Pauson, P. L. *J. Chem. Soc.* **1961**, 3475.

recrystallized from CH_2Cl_2/hexane to give **1b** as an orange solid. Yield: 0.56 g, 94%. IR: ν_{max} (CO)/cm^{-1} (hex), 1966 (vs), 1928 (s), and 1905 (s).

Tricarbonyl(7-*exo*-{dicarbomethoxymethyl}cycloheptatriene)chromium(0) (1c). A solution of Na[$(CH_3CO_2)_2CH$] was prepared by stirring dimethyl malonate (1.14 mL, 10 mmol) and NaH (1.2 equiv) in THF (50 mL) at room temperature for 30 min, followed by filtration through Celite. This solution was added dropwise to a suspension of tricarbonyl(η-cycloheptatrienyl)chromium hexafluorophosphate (2.7 g, 7.3 mmol) in THF (50 mL) at −78 °C, and the mixture was allowed to warm to room temperature over 1 h. Evaporation of the solvent in vacuo and chromatography on alumina, eluting with CH_2Cl_2/hexane (1:1), gave **1c** as a yellow solid. Yield: 1.94 g, 75%. **1c**: Anal. Calcd for $C_{15}H_{14}CrO_7$: C, 50.29; H, 3.94. Found: C, 50.23; H, 3.90. IR: ν_{max} (CO)/cm^{-1} (hex), 1966 (vs), 1927 (s), 1917 (s), and 1758 (m).

Tricarbonyl($\eta^{2:4}$-7,8-diphenylbicyclo[4.2.1]nona-2,4,7-triene)chromium(0) (2a). A solution of **1a** (0.200 g, 0.877 mmol) and diphenylacetylene (0.187 g, 1.05 mmol) in *n*-hexane (120 mL) was irradiated (Pyrex glassware) with UV light at 25 °C for 4.5 h. The product precipitated as purple crystals and the hexane was removed via cannula. Dissolution of the crystals in dichloromethane, filtration through alumina, and reprecipitation with *n*-hexane, including a reduction of the volume of the solution in vacuo if necessary, gave 0.300 g (85%) of **2a** as a purple crystalline solid. **2a**: Anal. Calcd for $C_{24}H_{18}CrO_3$: C, 70.93; H, 4.46. Found: C, 70.91; H, 4.26. IR: ν_{max} (CO)/cm^{-1} (hex), 1978 (vs), 1913 (vs), and 1887 (vs).

Tricarbonyl{$\eta^{2:4}$-7,8-bis(4-methylphenyl)bicyclo[4.2.1]nona-2,4,7-triene}chromium(0) (2b). A solution of **1a** (0.200 g, 0.877 mmol) and bis(4-methylphenyl)acetylene (0.250 g, 1.21 mmol) in toluene (100 mL) was irradiated (Pyrex glassware) with UV light at 0 °C for 20 h. Filtration through Celite, removal of the solvent in vacuo, and chromatography of the residue on alumina, eluting with *n*-hexane/CH_2Cl_2 (1:1), gave deep red crystals of the product following removal of the solvent. Yield: 0.327 g, 86%. **2b**: Anal. Calcd for $C_{26}H_{22}CrO_3$: C, 71.88; H, 5.10. Found: C, 72.08; H, 5.00. IR: ν_{max} (CO)/cm^{-1} (hex), 1979 (vs), 1913 (vs), and 1887 (vs).

Tricarbonyl{$\eta^{2:4}$-7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-2,4,7-triene}chromium(0) (2c). A solution of **1a** (0.100 g, 0.438 mmol) and bis(trimethylsilyl)acetylene (0.18 g, 0.24 mL, 1.05 mmol) in *n*-hexane (100 mL) was irradiated (Pyrex glassware) with UV light at 25 °C for 36 h. Filtration through Celite, removal of the solvent in vacuo, and chromatography of the residue on alumina, eluting with *n*-hexane/CH_2Cl_2 (19:1), gave an orange crystalline product following removal of the solvent. Yield: 0.139 g, 79.6%. Spectroscopic data for **2c** are identical to those previously reported.[4a]

Tricarbonyl{$\eta^{2:4}$-7,8-diethylbicyclo[4.2.1]nona-2,4,7-triene}chromium(0) (2d). A solution of **1a** (0.375 g, 1.53 mmol) and 3-hexyne (0.280 mL, 2.29 mmol) in toluene (120 mL) was irradiated (Pyrex glassware) with UV light at −20 °C for 20 h with a slow purge of carbon monoxide. Filtration through Celite, removal of the solvent in vacuo, and chromatography of the residue on silica, eluting with *n*-pentane/CH_2Cl_2 (1:1), gave orange crystals of the product following removal of the solvent. Yield: 0.144 g, 28%. **2d**: Anal. Calcd for $C_{16}H_{18}CrO_3$: C, 61.93; H, 5.85. Found: C, 61.66; H, 5.41. IR: ν_{max} (CO)/cm^{-1} (hex), 1970 (vs), 1898 (vs), and 1884 (vs).

Tricarbonyl[$\eta^{2:4}$-7,8-bis(trimethylsilyl)-9-phenylbicyclo[4.2.1]nona-2,4,7-triene]chromium(0) (2e). A solution of **1b** (0.104 g, 0.34 mmol) and bis(trimethylsilyl)acetylene (0.07 g, 0.4 mmol) in *n*-hexane (30 mL) was irradiated (Pyrex glassware) with UV light at 25 °C for 4 h. Filtration through Celite, removal of the solvent in vacuo, and chromatography of the residue on silica, eluting with *n*-hexane/CH_2Cl_2 (9:1), gave an orange oil following removal of the solvent. Recrystallization from CH_2Cl_2/hexane gave **2e** as an orange solid. Yield: 0.15 g, 94%. **2e**: Anal. Calcd for $C_{24}H_{30}CrO_3Si_2$: C, 60.75; H, 6.32. Found: C, 60.62; H, 6.66. IR: ν_{max} (CO)/cm^{-}11 (hex), 1965 (vs), and 1890 (vs).

Tricarbonyl[$\eta^{2:4}$-7,8-bis(trimethylsilyl)-9-(dicarbomethoxymethyl)-bicyclo[4.2.1]nona-2,4,7-triene]chromium(0) (2f). A solution of **1c** (0.37 g, 1.03 mmol) and bis(trimethylsilyl)acetylene (0.33 mL, 1.5 mmol) in toluene (50 mL) was irradiated (Pyrex glassware) with UV light at 25 °C for 3 days under a constant purge of CO. Filtration through Celite, removal of the solvent in vacuo, and chromatography of the residue on Florosil, eluting with *n*-hexane/CH_2Cl_2 (1:1), gave **2f** as a red oil following removal of the solvent. Recrystallization from *n*-hexane at −10 °C gave analytically pure **2f**. Yield: 0.275 g, 50%. **2f**: Anal. Calcd for $C_{23}H_{32}CrO_7Si_2$: C, 52.27; H, 6.06. Found: C, 52.34; H, 6.04. IR: ν_{max} (CO)/cm^{-1} (toluene), 1959 (vs), and 1882 (vs).

7,8-Diphenylbicyclo[4.2.1]nona-2,4,7-triene (3a). A deep purple solution of **2a** (0.180 g, 0.443 mmol) in toluene (20 mL) was refluxed for 5 min or until it turned pale yellow. The toluene was removed in vacuo, and the residue was purified on a TLC plate (Whatman PK6F silica gel 60 Å) to give **3a** as a white solid. Yield: 0.035 g, 29%. Spectroscopic data of **3a** were identical to those previously reported.[2]

7,8-Bis(4-methylphenyl)bicyclo[4.2.1]nona-2,4,7-triene (3b). This compound was prepared as for **3a** from **2b** (0.100 g, 0.230 mmol). Yield: 0.026 g, 38%. MS: *m/z* 298 (M^+), 283 ($M^+ - Me$), 268, 253, intensity 100 peak at 91.

7,8-Dicarbomethoxybicyclo[4.2.1]nona-2,4,7-triene (3g). A deep red solution of **1a** (0.100 g, 0.44 mmol) and DMAD (0.090 mL, 0.73 mmol) in toluene (50 mL) was irradiated with UV light through quartz under a slow purge of CO gas for 4 h at room temperature. The solution became turbid and pale yellow in color. Evaporation of the toluene in vacuo and chromatography (TLC, Whatman PK6F silica gel 60 Å), eluting with CH_2Cl_2, gave the product as an milky oil. Yield: 0.067 g (66% based on **1a**).

Tricarbonyl(η^6-7,8-diphenylbicyclo[4.2.1]nona-2,4,7-triene)chromium(0) (4). A solution of **2a** (0.420 g, 1.03 mmol) in CH_2Cl_2 (100 mL) was stirred at room temperature for 3 days, during which time the dark purple solution turned yellow. Filtration through Celite and removal of the solvent in vacuo, followed by chromatography on alumina eluting with *n*-hexane/CH_2Cl_2 (9:1), gave **4** as a yellow oil. Yield: 0.336 g, 80%. IR: ν_{max} (CO)/cm^{-1} (hex), 1979 (vs), and 1912 (vs).

Tricarbonyl{$\eta^{2:4}$-7,8-diphenyl-9-carbethoxy-9-azabicyclo[4.2.1]nona-2,4,7-triene}chromium(0) (6a). A solution of **5**[8] (0.436 g, 1.45 mmol) and diphenylacetylene (0.387 g, 2.18 mmol) in toluene (120 mL) was flushed thoroughly with carbon monoxide gas and then irradiated (Pyrex glassware) with UV light at −20 °C for 8 h. Filtration through Celite, removal of the solvent in vacuo, washing with *n*-hexane, and recrystallization from *n*-hexane/CH_2Cl_2 gave **6a** as brownish-red crystals. Yield: 0.436 g, 68%. **6a**: Anal. Calcd for $C_{26}H_{21}CrNO_5$: C, 65.13; H, 4.42; N, 2.92. Found: C, 64.88; H, 4.32; N, 2.84. IR: ν_{max} (CO)/cm^{-1} (hex), 1983 (vs), 1919 (vs), 1895 (vs), and 1720 (m).

Tricarbonyl{$\eta^{2:4}$-7,8-bis(trimethylsilyl)-9-carbethoxy-9-azabicyclo-[4.2.1]nona-2,4,7-triene}chromium(0) (6b). A solution of **5** (0.469 g, 1.56 mmol) and bis(trimethylsilyl)acetylene (0.662 g, 0.88 mL, 3.90 mmol) in *n*-hexane (120 mL) was irradiated (Pyrex glassware) with UV light at −20 °C for 10 h. Filtration through Celite, removal of the solvent in vacuo, and chromatography on Florosil, eluting with *n*-hexane/CH_2Cl_2/acetone (50:45:5), gave **6b** as an orange crystalline solid after evaporation of the solvents. Yield: 0.461 g, 63%. **6b**: Anal. Calcd for $C_{20}H_{29}CrNO_5Si_2$: C, 50.94; H, 6.20; N, 2.97. Found: C, 51.23; H, 6.37; N, 2.71. IR: ν_{max} (CO)/cm^{-1} (hex), 1970 (vs), 1896 (vs), and 1723 (m).

7,8-Diphenyl-9-carbethoxy-9-azabicyclo[4.2.1]nona-2,4,7-triene (7a). A deep purple solution of **6a** (0.168 g, 0.35 mmol) in toluene (20 mL) was refluxed for 5 min or until it turned pale yellow. The toluene was removed in vacuo and the residue purified (TLC, silica, elutate hexane/CH_2Cl_2 1:1) to give **7a** as a clear oil. Yield: 0.106 g, 88%. **7a**: exact mass found *m/z* 343.1573 (M^+), calcd for $C_{23}H_{21}NO_2$ 343.1572.

7,8-Bis(trimethylsilyl)-9-carbethoxy-9-azabicyclo[4.2.1]nona-2,4,7-triene (7b). A solution of complex **6b** (0.150 g, 0.32 mmol) and excess iodine in toluene (20 mL) was refluxed for 5 min. The toluene was removed in vacuo and the residue purified (TLC, silica, eluate hexane/CH_2Cl_2 1:3) to give **7b** as a clear oil, yield 0.090 g, 84%. **7b**: exact mass found *m/z* 335.1730 (M^+), calcd for $C_{17}H_{29}NO_2Si_2$ 335.1737.

Isolation of Complex 8. Complex **8** is isolated as a byproduct from the reaction of impure **5** and alkynes. It was eluted from the Florosil column using acetone/CH_2Cl_2 (1:1) following the adducts **6a,b** and was recrystallized from CH_2Cl_2/hexane as a pure orange crystalline solid. **8**: Anal. Calcd for $C_{21}H_{22}CrN_2O_7$: C, 54.03; H, 4.72; N, 6.00.

Found: C, 53.71; H, 4.49; N, 5.77. IR: ν_{max} (CO)/cm^{-1} (hex), 1989 (vs), 1820 (s), 1814 (s), and 1734 (m).

Thermally Induced Metal-Catalyzed 6 + 2 Cycloadditions. 7,8-Bis(trimethylsilyl)bicyclo[4.2.1]nona-2,4,7-triene (3c). Method A. A solution of hexacarbonylchromium(0) (0.39 g, 1.8 mmol), 1,3,5-cycloheptatriene (1.62 g, 18 mmol) and bis(trimethylsilyl)acetylene (3.00 g, 18 mmol) in dibutyl ether (2 mL) was refluxed under nitrogen for 48 h. The solvent was removed in vacuo to give a viscous brown residue which was dissolved in CH_2Cl_2 (2 mL) and chromatographed on a silica gel column (2 × 30 cm), eluting with 4:1 *n*-hexane/CH_2Cl_2. Evaporation of the solvent gave a yellow oily liquid **3c**. Yield: 2.99 g, 65%. ^{1}H NMR and ^{13}C{^{1}H} NMR data were identical to those reported in the literature.[4a]

Method B. A solution of diiron nonacarbonyl (0.43 g, 1.2 mmol), 1,3,5-cyclopheptatriene (1.08 g, 12 mmol), and bis(trimethylsilyl)acetylene (2.00 g, 12 mmol) in dibutyl ether (2 mL) was refluxed under nitrogen for 48 h. Workup as in **A** above gave **3c** as a yellow oily liquid. Yield: 1.46 g, 47%.

7,8-Diethylbicyclo[4.2.1]nona-2,4,7-triene (3d). A solution of hexacarbonylchromium(0) (0.54 g, 2.4 mmol), 1,3,5-cycloheptatriene (2.24 g, 24 mmol), and 3-hexyne (2.00 g, 24 mmol) in dibutyl ether (2 mL) was refluxed under nitrogen for approximately 3 days. The resulting deep red solution was reduced in volume in vacuo, dissolved in CH_2Cl_2 (2 mL), and chromatographed on a silica gel column (2 × 30 cm), eluting with *n*-hexane. Evaporation of the solvent gave a red oily liquid (**3d**) that contains a trace amount of **1a**. **3d.** Yield: 2.10 g, 47%. MS: 174 (M^+), 159 ($M^+ - CH_3$), 145 ($M^+ - CH_2CH_3$).

7,8-Dimethylbicyclo[4.2.1]nona-2,4,7-triene (3h). A solution of hexacarbonylchromium(0) (0.20 g, 0.92 mmol), 1,3,5-cycloheptatriene (0.85 g, 9.2 mmol), and 2-butyne (0.50 g, 9.2 mmol) in dibutyl ether (1 mL) was refluxed under nitrogen for 48 h. The resulting brownish black solution was reduced in volume in vacuo, dissolved in CH_2Cl_2 (2 mL), and chromatographed on a silica gel column (2 × 30 cm), eluting with *n*-hexane. Evaporation of the solvent in vacuo afforded a yellow oily liquid **3h**. Yield: 1.09 g, 81%. Exact mass found: *m/z* 146.1094 (M^+), calcd for $C_{11}H_{14}$ 146.1096.

***exo*-Dimethyl Tricyclo[3.2.2.0^{2,4}]nona-6,8-diene-6,7-dicarboxylate (9).** A solution of hexacarbonylchromium(0) (0.76 g, 3.5 mmol), 1,3,5-cycloheptatriene (3.24 g, 35 mmol), and dimethyl acetylenedicarboxylate (5.00 g, 35 mmol) in toluene (10 mL) was refluxed under nitrogen for 3 days. The solvent was removed in vacuo, and diethyl ether (50 mL) was added to the residue. The yellow solution was filtered through Celite and reduced in volume. The residue was dissolved in CH_2Cl_2 (3 mL) and chromatographed on a silica gel column (2 × 60 cm), eluting with 2:1 *n*-hexane/CH_2Cl_2. Evaporation of the solvent in vacuo gave a yellow oily liquid (**9**). Yield: 3.34 g, 40%. ^{1}H NMR spectral data for **9** were identical to those reported in the literature[11] and indicated that the sample was contaminated with a trace amount (<5%) of the known byproduct dimethyl bicyclo[3.2.2]nona-2,6,8-triene-2,3-dicarboxylate.[11] **9**: exact mass found *m/z* 234.0890 (M^+), calcd for $C_{13}H_{14}O_4$ 234.0892.

X-ray Diffraction Study of 6b (University of Delaware). Crystallographic data are collected in Table 4. A crystal (ruby red block) of dimensions 0.34 × 0.40 × 0.52 mm was selected from a sample grown from a CH_2Cl_2/hexane solution at −5 °C for 2 days. The assigned crystal system was confirmed by photographic methods, and the space group was uniquely determined by systematic absences in the diffraction data. Data were collected on a Siemens P4 diffractometer at 235 K. Of 3063 data collected ($4° < 2\theta < 45°$), 3063 were independent and 2500 were observed with $F \geq 4\sigma(F)$. Azimuthal scans about the diffraction vector showed a variation of less than 10%; accordingly, no correction for absorption was applied. Autointerpreted Patterson synthesis was used to locate the heavy atom. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were treated as idealized contributions. All computations used the SHELXTL program library (PC version 4.2, G. Sheldrick, Siemens, Madison, WI).

X-ray Diffraction Study of 8 (Rutgers University). Crystallographic data are collected in Table 4. A crystal (orange parallelepiped) of dimensions 0.08 × 0.28 × 0.28 mm was selected from a sample grown from a CH_2Cl_2/hexane solution at −10 °C for 7 days and mounted inside a glass capillary under nitrogen. Fifteen high-angle reflections were used to calculate the orientation matrix and best cell dimensions. The assigned crystal system and space group were uniquely determined by systematic absences in the diffraction data. Data were collected on a Siemens P4 diffractometer at 297 K with a graphite monochromator using Mo Kα radiation with three check reflections recorded every 47 reflections. A total of 2192 unique reflections were measured in the $\theta-2\theta$ scan mode ($3.0° < 2\theta < 42.0°$), of which 1044 had $F > 4\sigma(F)$ which were used in the refinement. Empirical absorption corrections (ψ-scans) were made. Autointerpreted Patterson synthesis was used to locate the heavy atom. All non-hydrogen atoms were found in difference electron density maps and were anisotropically refined. Hydrogen atoms were calculated and treated as idealized riding model contributions. Final difference electron density maps showed no features outside the range 0.38 to −0.37 e Å^{-3}. All computations used the PC SHELXTL program library (version 4.21, G. Sheldrick, Siemens, Madison, WI).

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Supplementary Material Available: Complete tables of X-ray structural data, positional parameters, anisotropic thermal parameters, bond lengths and angles for compounds **6b** and **8** (17 pages); tables of observed and calculated structure factors (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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