CYCLOADDITION REACTIONS OF (η^6-TROPONE)TRICARBONYLMETAL(0) COMPLEXES OF GROUP 6 METALS WITH ALKYNES

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(η^6-Cyclohepta-2,4,6-trien-1-one)tricarbonylmetal(0) complexes of chromium (**2a**), molybdenum (**2b**), and tungsten (**2c**) are formed when tris(acetonitrile)tricarbonylchromium(0), -molybdenum(0), and -tungsten(0), respectively, are treated photochemically with tropone (cyclohepta-2,4,6-trien-1-one) **1**. UV photolysis of **2a**–**2c** and RC≡CR′ (R = R′ = Ph, Me$_3$Si, Et; R = Ph, R′ = Me$_3$Si) in toluene gives the [6+2] cycloadducts, (η^4,η^2-8,9-diphenylbicyclo-[4.2.1]nona-3,5,8-trien-1-one)tricarbonylmetal(0) **3a**–**3c**, (η^4,η^2-8,9-bis(trimethylsilyl)bicyclo-[4.2.1]nona-3,5,8-trien-1-one)tricarbonylmetal(0) **4a**–**4c**, (η^4,η^2-8,9-diethylbicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonylmetal(0) **5a**–**5c**, and (η^4,η^2-8-phenyl-9-(trimethylsilyl)bicyclo-[4.2.1]nona-3,5,8-trien-1-one)tricarbonylmetal(0) **6a**–**6c**. Compounds **2a**–**2c**, **3a**–**3c**, **4a**–**4c**, **5a**–**5c**, and **6a**–**6c** were purified by chromatography, recrystallized and isolated as analytically pure crystalline solids in moderate yields and characterized by mass, IR, and NMR spectroscopy. Pure organic heterobicyclotriene ligands **7a**, **8a**, **9a**, and **10a** were isolated from **3a**, **4a**, **5a**, and **6a**, respectively, by treatment with cerium(IV) ammonium nitrate (R = R′ = Me$_3$Si; R = Ph, R′ = Me$_3$Si) or by heating in toluene (R = R′ = Ph, Et). It was not possible to isolate the bicyclic complexes resulting from the reactions of **2a**–**2c** with terminal alkynes like phenylacetylene.

Keywords: Tropone; [6+2] Cycloadditions; Chromium complexes; Photochemical synthesis; Molybdenum complexes; Alkynes; Bicyclo[4.2.1]nona-3,5,8-trien-1-ones.

Transition-metal-mediated high-order cycloaddition reactions of unsaturated organic substrates to coordinated cyclopolyenes is of potential synthetic value as it provides access to oligocyclic adducts, which may be difficult to produce by conventional multistep synthesis. The reactions were first reported by Pettit *et al.*[1] for iron species and later by Kreiter[2–5] using chromium. In addition, other isolated complexes have appeared in the literature over the years[6–9]. More recently, Rigby has smartly applied these and other new metal-promoted cycloadditions to a variety of synthetic problems[10–13]. The advent of effective photochemically, metal-promoted versions of these transformations has provided convenient access to a num-

ber of highly substituted bicyclo[4.4.1]undecane and bicyclo[4.2.1]nonane systems in diastereomerically pure forms[14–17]. These so-called high-order cycloaddition reactions (6+2, 6+4, 4+4) are typically characterized by a high level of stereoselectivity and relatively low chemical efficiency. The chemistry of 1*H*-azepine and its *N*-substituted complexes has also been known for a long time[18–22]. In earlier reports we presented preliminary results of the photoinduced [6+2] and [6+2] cycloadditions of alkynes to (η^6-azepine-1-carbonitrile)tricarbonylchromium(0) which ultimately gave bicyclo[4.2.1]-nona-2,4,7-triene[23]. Tropone (cyclohepta-2,4,6-trien-1-one) has emerged as one of the more effective 6π participants in high-order cycloaddition reactions[24,25]. This ligand participates in a thermally allowed [6+4] cycloaddition with a limited range of dienes to provide adducts in modest yields[27]. We now present complete details of the photochemical synthesis of (η^6-cyclohepta-2,4,6-trien-1-one)tricarbonylmetal(0) complexes **2a–2c** (M = Cr, Mo, W; Scheme 1), their new [6+2] cycloadditions (Scheme 2) with alkynes leading to tricarbonylmetal(0) complexes **3a–3c**, **4a–4c**, **5a–5c**, and **6a–6c**, as well as decomplexation to bicyclononatrienes **7a**, **8a**, **9a**, and **10a** (Scheme 3).
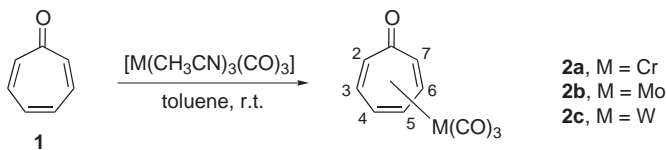

SCHEME 1

RESULTS AND DISCUSSION

UV irradiation of [M(CH$_3$CN)$_3$(CO)$_3$] (M = Cr, Mo, W) in the presence of tropone **1** leads to the formation of complexes **2a–2c** (Scheme 1), and the UV irradiation of hexane solutions of [M(η^6-C$_7$H$_6$O)(CO)$_3$] (M = Cr, Mo, W) **2a–2c** in the presence of diphenylacetylene, bis(trimethylsilyl)acetylene, diethylacetylene or 1-phenyl-2-(trimethylsilyl)acetylene leads to the formation of adducts **3a–3c**, **4a–4c**, **5a–5c**, and **6a–6c**, respectively, as a result of [6+2] cycloadditions of an alkyne to the metal-coordinated tropone (Scheme 2).

Experiments dealing with the photolysis of complexes **2a–2c** with phenylacetylene (PhC≡CH) was not successful in this work. Eventhough the IR spectral changes during irradiation confirms the cycloaddition occurance, the long irradiation time (*ca* 25 h) makes the reaction mixture

to decompose. Therefore it was not possible to isolate these complexes as pure crystals for spectroscopic structural analysis.
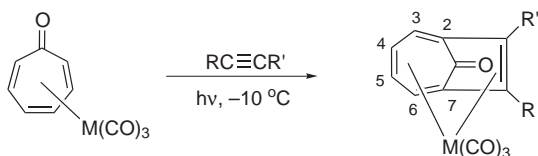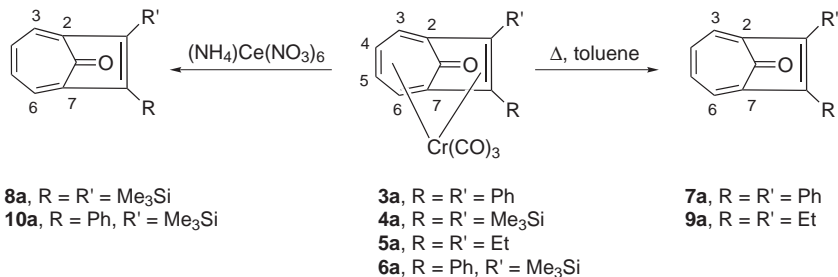

	R	R'	M
3a	Ph	Ph	Cr
3b	Ph	Ph	Mo
3c	Ph	Ph	W
4a	Me$_3$Si	Me$_3$Si	Cr
4b	Me$_3$Si	Me$_3$Si	Mo
4c	Me$_3$Si	Me$_3$Si	W
5a	Et	Et	Cr
5b	Et	Et	Mo
5c	Et	Et	W
6a	Ph	Me$_3$Si	Cr
6b	Ph	Me$_3$Si	Mo
6c	Ph	Me$_3$Si	W

SCHEME 2

The composition and the structure of the complexes **2a**–**2c**, [M(η^6-cyclohepta-2,4,6-trien-1-one)(CO)$_3$], **3a**–**3c**, [M(η^4,η^2-8,9-diphenylbicyclo-[4.2.1]nona-3,5,8-trien-1-one)(CO)$_3$], **4a**–**4c**, [M(η^4,η^2-8,9-bis(trimethyl-silyl)bicyclo[4.2.1]nona-3,5,8-trien-1-one)(CO)$_3$], **5a**–**5c**, [M(η^4,η^2-8,9-diethyl-bicyclo[4.2.1]nona-3,5,8-trien-1-one)(CO)$_3$], and **6a**–**6c**, [M(η^4,η^2-8-phenyl-9-(trimethylsilyl)bicyclo[4.2.1]nona-3,5,8-trien-1-one)(CO)$_3$] are established on the basis of elemental analysis, mass, IR, and NMR spectroscopic data.

Moreover, the bicyclo[4.2.1]nona-3,5,8-trien-1-one ligands **7a**, **8a**, **9a**, and **10a** can be readily released from the metal complex (Scheme 3). Thus if

8a, R = R' = Me$_3$Si
10a, R = Ph, R' = Me$_3$Si

3a, R = R' = Ph
4a, R = R' = Me$_3$Si
5a, R = R' = Et
6a, R = Ph, R' = Me$_3$Si

7a, R = R' = Ph
9a, R = R' = Et

SCHEME 3

a toluene solution of **3a** or **5a** is refluxed for 15–30 min, a ligand exchange occurs forming **7a**, **9a**, and (η^6-toluene)tricarbonylmetal(0). The complexes **4a** or **6a** are more robust; an oxidative decomposition with ammonium cerium(IV) nitrate is required to release the compounds **8a** and **10a**. The pure organic compounds **7a**, **8a**, **9a**, and **10a** were isolated (TLC on silica) as colorless oils and characterized by mass and NMR spectroscopy. Compounds **7a**, **8a**, **9a**, and **10a** show no unusual features in their ^{1}H or ^{13}C NMR spectra and thus provide more compelling evidence of the identity of their complexes **3a**–**3c**, **4a**–**4c**, **5a**–**5c**, and **6a**–**6c**.

The IR spectra of complexes **2a**–**2c** in hexane solutions exhibit three strong absorption bands in the CO-stretching region with approximately equal intensities consistent with the expected *fac*-structure of the $M(CO)_3$ moiety. An additional band is observed for the C=O bond which shows no significant shift upon coordination. The appearance of three CO stretching bands of equal intensities indicates a structure of C_1 or C_s symmetry. Furthermore, the number of signals in both the ^{1}H and ^{13}C{^{1}H} NMR spectra of **2a**–**2c** indicates a structure with C_s symmetry. The ^{1}H NMR spectra of complexes **2a**–**2c** in CDCl$_3$ exhibit three multiplets with relative intensities 1 : 1 : 1 which are assigned for $H_{2,7}$, $H_{3,6}$, and $H_{4,5}$ with large significant chemical shifts from those of the free tropone ligand (δ ppm, $H_{2,7}$ 5.57, $H_{3,6}$ 5.34, $H_{4,5}$ 5.96) to higher magnetic fields indicating the η^6-π-coordination of the tropone ligand to the metal atom. The ^{13}C{^{1}H} NMR spectra of complexes **2a**–**2c** recorded from their deuterated toluene solutions show the appearance of a singlet for each pair of carbons, $C_{2,7}$, $C_{3,6}$, $C_{4,5}$. These singlets exhibit a large shift to higher magnetic field compared with the free tropone ligand (δ ppm, $C_{2,7}$ 126.14, $C_{3,6}$ 118.43, $C_{4,5}$ 124.81) upon coordination of the metal atom indicating the formation of the η^6-π-coordination complexes. One singlet of the C=O group is also observed at 175.80 ppm which shows no significant shift upon coordination. In addition, two signals of relative intensities 2 : 1 are observed in the CO region assigned to the $M(CO)_3$ carbonyl groups. The appearance of a multiplet for each pair of hydrogens ($H_{2,7}$, $H_{3,6}$, $H_{4,5}$) in the ^{1}H NMR as well as a singlet for each pair of carbon atoms ($C_{2,7}$, $C_{3,6}$, $C_{4,5}$) and two singlets of relative intensities 2 : 1 for carbonyl groups in the ^{13}C{^{1}H} NMR spectra of these complexes confirms the formation of the η^6-π-complexes without disturbing the symmetry of the tropone ligand to form complexes of C_s symmetry.

The IR spectra of complexes **3a**–**3c**, **4a**–**4c**, **5a**–**5c**, and **6a**–**6c** in hexane solutions exhibit three strong bands in the CO stretching region with relative intensities consistent with the expected *fac*-structure of the $M(CO)_3$

moiety indicating a structure with C_1 or C_s symmetry. These bands are shifted towards lower frequencies compared with those of complexes **2a**–**2c**. An additional band is observed for the CO group of the tropone ligand with no significant shift. The ^{1}H NMR spectra of complexes **3a**–**3c**, **4a**–**4c**, and **5a**–**5c** in CDCl$_3$ solutions exhibit three multiplets, with relative intensities 2 : 2 : 2 which are assigned to each pair of hydrogen atoms of the tropone ring. These multiplets show small shifts toward higher magnetic field compared with those of complexes **2a**–**2c**. A singlet associated with the 18 protons of the trimethylsilyl groups in complexes **3a**–**3c**, a multiplet associated with the phenyl groups in complexes **4a**–**4c**, and two multiplets associated with the ethyl groups in complexes **5a**–**5c** are also observed. The ^{1}H NMR spectra of the complexes **6a**–**6c** in CDCl$_3$ show multiplets for the protons H$_{2,7}$, H$_{3,6}$, and H$_{4,5}$. In addition, a singlet belonging to the 18 protons of the Me$_3$Si group and a multiplet to the phenyl group protons are also observed. These spectra show some a symmetry in the bicyclic ring that is not observed in the complexes **3a**–**3c**, **4a**–**4c**, or **5a**–**5c** analogs. Thus the ^{1}H NMR spectra of **6a**–**6c** show two doublets for H2 and H7. On the other hand, the ^{13}C{^{1}H} NMR spectra of the complexes **3a**–**3c**, **4a**–**4c**, and **5a**–**5c** recorded from their deuterated toluene solutions also show four singlets which are assigned to each pair of carbon atoms (C$_{2,7}$, C$_{3,6}$, C$_{4,5}$, C$_{8,9}$) of the bicyclic system. A multiplet for the phenyl groups in complexes **3a**–**3c**, one singlet for the trimethylsilyl groups in complexes **4a**–**4c**, and two singlets for the ethyl groups in complexes **5a**–**5c** are also observed. In addition, two singlets of relative intensities 2 : 1 are observed in the CO region assigned to the M(CO)$_3$ carbonyl groups. The appearance of only one multiplet for each pair of hydrogen atoms in the ^{1}H NMR spectra, only one singlet for each pair of carbons of the tropone ring and two singlets in the CO region in the ^{13}C{^{1}H} NMR spectra of these complexes is an indication of the existence of a plane of symmetry which confirms a structure of C_s symmetry. The ^{13}C{^{1}H} NMR spectra of the complexes **6a**–**6c** in deuterated toluene solutions show eight unique signals for carbons 2 through 9 of the heterobicyclic ring. A multiplet for the phenyl group and a singlet for the trimethylsilyl group are also observed. In addition, three singlets of equal intensities are observed in the CO region of these spectra. The splitting of the ^{1}H NMR signals, the appearance of eight unique singlets for each carbon atom of the bicyclic ring, and three singlets of equal intesities in the CO region in the ^{13}C{^{1}H} NMR spectra is an indication of some asymmetry in the bicyclic ring which confirms a structure of C_1 symmetry of complexes **6a**–**6c**. The large chemical shift difference in the singlets of C2 and C7 confirms the occurrence of cycloaddition of the

alkyne to the carbon atoms 2 and 7 of the tropone ring. This new bicyclic ligand can offer a chelate by metal coordination to η^4-C3–C6 and for η^2-C8–C9.

The ^{1}H and ^{13}C{^{1}H} NMR data of the free organic ligands **7a**, **8a**, **9a**, and **10a** are in reasonably good accord with their structures (Scheme 3). The chemical shifts of some atoms (in particular the diene part) are significantly different from those of complexes **3a**, **4a**, **5a**, and **6a** due to the absence of upfield coordination shifts which are effective in the metal-coordinated complexes. A comparison of ^{13}C{^{1}H} NMR spectra of **7a**, **8a**, **9a**, **10a** and **3a**, **4a**, **5a**, **6a** likewise reveals characteristic coordination shifts of the C=C carbon atoms.

CONCLUSION

Study of reactions of group 6 metals with tropone (cyclohepta-2,4,6-trien-1-one) and carbonyl ligands has attracted our interest, due to their multi-bonding probability. Several high-order cycloaddition reactions can be promoted by those complexes. The [6+2] cycloaddition reactions can be performed with a variety of disubstituted (but not with terminal) alkynes under photochemical activation using stoichiometric amounts of complexes **2a**–**2c**. Photolysis of complexes **2a**–**2c** in the presence of alkynes leads to heterobicyclic adducts as a result of the [6+2] cycloaddition. Decomplexation of the pure bicyclic organic ligands **7a**, **8a**, **9a**, and **10a** was important in this work since it provides more compelling evidence for the identity of the organometallic complexes **3a**–**3c**, **4a**–**4c**, **5a**–**5c**, and **6a**–**6c**.

EXPERIMENTAL

General Comments

The preparations and reactions of all complexes were performed under dry and deoxygenated nitrogen gas using standard Schlenck techniques. The solvents used were purified by refluxing over metallic sodium or anhydrous phosphorus pentoxide under nitrogen for a period of four to five days prior to use. The reagents and chemicals were purchased from Merck GmbH, Germany or Aldrich and used without further purification. The photochemical reactions and other treatments were followed by IR spectra taken at appropriate time intervals.

IR spectra (wavenumbers in cm^{-1}) were recorded in dichloromethane or hexane solutions on a Jasco 430 RT-IR spectrophotometer (400–4000 cm^{-1}). ^{13}C NMR spectra were recorded from deuterated toluene solutions on a Bruker AMX 400 FT NMR spectrometer at 100.62 MHz. ^{1}H NMR spectra were recorded in CDCl$_3$ solutions on a Bruker WP 200 at 200 MHz. Chemical shifts (δ, ppm) are given relative to internal tetramethylsilane, TMS. Coupling

constants (*J*) are given in Hz. The assignment of NMR signals is based on ^1H and $^{13}C\{^1H\}$ spectra. Elemental analysis was carried out on a HP 185 CNH analyzer. Mass spectra were taken on a Varian MAT 311 Instrument. Chromatography was performed on silica gel 230–425 mesh. Tris(acetonitrile)tricarbonylmetal(0) complexes[27] were prepared using the literature procedures.

Synthesis of the Complexes (η⁶-Cyclohepta-2,4,6-trien-1-one)tricarbonylmetal(0). General Procedure

A solution of 1.0 g of $[M(CH_3CN)_3(CO)_3]$, M = Cr (3.86 mmol), Mo (3.30 mmol), W (2.56 mmol), and 1.0 g of tropone (0.91 ml, 9.43 mmol) in toluene (150 ml) was irradiated for 210, 185 and 150 min, respectively, with a high-pressure mercury lamp (Hg-Tauchlampe TQ 150 W, Quarzlampen GmbH, Hanau, Germany) which is housed in a water-cooled glass jacket. The resulting dark solution is filtered and then evaporated under high vacuum (0.01 mm Hg). The residue is then purified by recrystallization from pentane at –70 °C. The obtained red crystals are best dried under vacuum for about 7 h and stored under nitrogen atmosphere for routine analysis.

(η⁶-Cyclohepta-2,4,6-trien-1-one)tricarbonylchromium(0) (**2a**). Yield 0.6 g (64% relative to [Cr(CH₃CN)₃(CO)₃]). Orange red solid, m.p. 78 °C. M.w.: 242 (MS). IR (hexane): ν(CO) 1998 vs, 1973 vs, 1906 s, 1583 m. ^1H NMR (CDCl₃): 4.86 d, 2 H, *J* = 8.6 (H₂,₇); 4.70 m, 2 H (H₃,₆); 5.87 m, 2 H (H₄,₅). $^{13}C\{^1H\}$ NMR (toluene-*d₈*): 84.93 (C₂,₇); 96.22 (C₃,₆); 101.24 (C₄,₅); 175.80 (C=O); 226.1, 232.12 (M-CO). For C₁₀H₆CrO₄ (242.2) calculated: 49.6% C, 2.50% H; found: 49.76% C, 2.57% H.

(η⁶-Cyclohepta-2,4,6-trien-1-one)tricarbonylmolybdenum(0) (**2b**). Yield 0.7 g (74% relative to [Mo(CH₃CN)₃(CO)₃]). Orange red solid, m.p. 76 °C. M.w.: 286 (MS). IR (hexane): ν(CO) 1990 vs, 1973 vs, 1905 s, 1583 m. ^1H NMR (CDCl₃): 4.92 d, 2 H, *J* = 8.4 (H₂,₇); 4.70 m, 2 H (H₃,₆); 5.89 m, 2 H (H₄,₅). $^{13}C\{^1H\}$ NMR (toluene-*d₈*): 84.76 (C₂,₇); 96.48 (C₃,₆); 101.82 (C₄,₅); 175.76 (C=O); 226.53, 232.28 (M-CO). For C₁₀H₆MoO₄ (286.2) calculated: 41.97% C, 2.11% H; found: 41.61% C, 2.04% H.

(η⁶-Cyclohepta-2,4,6-trien-1-one)tricarbonyltungsten(0) (**2c**). Yield 0.6 g (62% relative to [W(CH₃CN)₃(CO)₃]). Orange red solid, m.p. 75 °C. M.w.: 374 (MS). IR (hexane): ν(CO) 1989 vs, 1969 vs, 1902 s, 1586 m. ^1H NMR (CDCl₃): 4.91 d, 2 H, *J* = 8.4 (H₂,₇); 4.76 m, 2 H (H₃,₆); 5.81 m, 2 H (H₄,₅). $^{13}C\{^1H\}$ NMR (toluene-*d₈*): 85.16 (C₂,₇); 96.86 (C₃,₆); 101.80 (C₄,₅); 175.83 (C=O); 227.38, 232.90 (M-CO). For C₁₀H₆WO₄ (374.1) calculated: 32.11% C, 1.62% H; found: 32.23% C, 1.68% H.

(η⁴,η²-8,9-Diphenylbicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonylmetals(0)

A solution of **2a**–**2c** [0.5 g: **2a** (2.07 mmol), **2b** (1.75 mmol), **2c** (1.34 mmol)] and diphenylacetylene (0.5 g, 3.24 mmol) in toluene (150 ml) was irradiated for 500, 450 and 410 min, respectively, at 263 K with a high-pressure mercury lamp. The residue was then filtered through Celite and the solvent evaporated *in vacuo*. Recrystallization from pentane–dichloromethane (5 : 1) and drying the residue under high vacuum produced a dark red crystals which were stored under nitrogen atmosphere.

(η⁴,η²-8,9-Diphenylbicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonylchromium(0) (**3a**). Yield 0.7 g (81% relative to **2a**). Red solid, m.p. 146 °C. M.w.: 420 (MS). IR (hexane): ν(CO) 1975 vs, 1943 vs, 1726 s, 1585 m. ^1H NMR (CDCl₃): 5.34 m, 2 H (H₂,₇); 4.92 m, 2 H (H₄,₅); 4.41 m,

2 H (H$_{3,6}$); 7.26 m, 6 H (Ph); 7.64 m, 4 H (Ph). ^{13}C{^{1}H} NMR (toluene-d_8): 72.16 (C$_{2,7}$); 79.42 (C$_{3,6}$); 86.92 (C$_{8,9}$); 98.34 (C$_{4,5}$); 127.6, 128.1, 129.0, 129.9, 130.8, 131.3 (Ph); 175.72 (C=O); 226.91, 231.360 (M-CO). For C$_{24}$H$_{16}$CrO$_4$ (420.4) calculated: 68.57% C, 3.84% H; found: 68.32% C, 3.68% H.

(η^4,η^2-8,9-Diphenylbicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonylmolybdenum(0) (**3b**). Yield 0.6 g (74% relative to **2b**). Red solid, m.p. 142 °C. M.w.: 463 (MS). IR (hexane): ν(CO) 1978 vs, 1942 vs, 1728 s, 1582 m. ^{1}H NMR (CDCl$_3$): 5.41 m, 2 H (H$_{2,7}$); 4.90 m, 2 H (H$_{4,5}$); 4.46 m, 2 H (H$_{3,6}$); 7.26 m, 6 H (Ph); 7.66 m, 4 H (Ph). ^{13}C{^{1}H} NMR (toluene-d_8): 72.35 (C$_{2,7}$); 79.46 (C$_{3,6}$); 86.85 (C$_{8,9}$); 98.45 (C$_{4,5}$); 127.1, 127.6, 128.1, 129.9, 130.8, 131.3 (Ph); 175.81 (C=O); 227.32, 231.85 (M-CO). For C$_{24}$H$_{16}$MoO$_4$ (463.3) calculated: 62.08% C, 3.47% H; found: 62.31% C, 3.59% H.

(η^4,η^2-8,9-Diphenylbicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonyltungsten(0) (**3c**). Yield 0.5 g (68% relative to **2c**). Red solid, m.p. 140 °C. M.w.: 552 (MS). IR (hexane): ν(CO) 1977 vs, 1940 vs, 1725 s, 1583 m. ^{1}H NMR (CDCl$_3$): 5.41 m, 2 H (H$_{2,7}$); 4.94 m, 2 H (H$_{4,5}$); 4.45 m, 2 H (H$_{3,6}$); 7.22 m, 6 H (Ph); 7.68 m, 4 H (Ph). ^{13}C{^{1}H} NMR (toluene-d_8): 72.30 (C$_{2,7}$); 79.48 (C$_{3,6}$); 86.80 (C$_{8,9}$); 89.43 (C$_{4,5}$); 127.9, 128.2, 129.3, 129.8, 130.6, 131.1 (Ph); 175.79 (C=O); 227.10, 232.30 (M-CO). For C$_{24}$H$_{16}$O$_4$W (552.2) calculated: 52.20% C, 2.92% H; found: 52.43% C, 3.02% H.

(η^4,η^2-8,9-Bis(trimethylsilyl)bicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonylmetals(0)

A solution of **2a**–**2c** [0.5 g: **2a** (2.07 mmol), **2b** (1.75 mmol), **2c** (1.34 mmol)] and bis(trimethylsilyl)acetylene (0.66 g, 0.88 ml, 3.90 mmol) in toluene (150 ml) was irradiated for 690, 620 and 590 min, respectively, at 263 K with a high-pressure mercury lamp. The resulting solution was then filtered through Celite and the solvent evaporated *in vacuo*. The dark brown residue was then chromatographed on silica gel using hexane–dichloromethane–acetone (10 : 9 : 1) mixture. The red eluate was collected and evaporated *in vacuo*. The resulting residue was then recrystallized from pentane by cooling at –78 °C overnight. Decantation of the solvent and drying the residue *in vacuo* produces the dark red crystals which were collected and stored under nitrogen.

(η^4,η^2-8,9-Bis(trimethylsilyl)bicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonylchromium(0) (**4a**). Yield 0.7 g (82% relative to **2a**). Red solid, m.p. 138 °C. M.w.: 412 (MS). IR (hexane): ν(CO) 1965 vs, 1928 vs, 1723 s, 1584 m. ^{1}H NMR (CDCl$_3$): 0.41 s (Me$_3$Si); 4.80 m, 2 H (H$_{2,7}$); 4.75 m, 2 H (H$_{4,5}$); 3.75 m, 2 H (H$_{3,6}$). ^{13}C{^{1}H} NMR (toluene-d_8): 1.0 (Me$_3$Si); 71.86 (C$_{2,7}$); 75.21 (C$_{3,6}$); 76.93 (C$_{8,9}$); 94.37 (C$_{4,5}$); 175.76 (C=O); 227.60, 231.90 (M-CO). For C$_{18}$H$_{24}$CrO$_4$Si$_2$ (412.5) calculated: 52.40% C, 5.86% H; found: 52.58% C, 5.98% H.

(η^4,η^2-8,9-Bis(trimethylsilyl)bicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonylmolybdenum(0) (**4b**). Yield 0.7 g (88% relative to **2b**). Red solid, 136 °C. M.w.: 456 (MS). IR (hexane): ν(CO) 1968 vs, 1930 vs, 1720 s, 1586 m. ^{1}H NMR (CDCl$_3$): 0.40 s (Me$_3$Si); 4.82 m, 2 H (H$_{2,7}$); 4.79 m, 2 H (H$_{4,5}$); 3.72 m, 2 H (H$_{3,6}$). ^{13}C{^{1}H} NMR (toluene-d_8): 1.1 (Me$_3$Si); 71.84 (C$_{2,7}$); 75.30 (C$_{3,6}$); 76.96 (C$_{8,9}$); 94.41 (C$_{4,5}$); 175.72 (C=O); 226.40, 231.30 (M-CO). For C$_{18}$H$_{24}$MoO$_4$Si$_2$ (456.3) calculated: 47.37% C, 5.30% H; found: 47.12% C, 5.19% H.

(η^4,η^2-8,9-Bis(trimethylsilyl)bicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonyltungsten(0) (**4c**). Yield 0.6 g (81% relative to **2c**). Red solid, m.p. 134 °C. M.w.: 554 (MS). IR (hexane): ν(CO) 1968 vs, 1926 vs, 1721 s, 1587 m. ^{1}H NMR (CDCl$_3$): 0.41 s (Me$_3$Si); 4.85 m, 2 H (H$_{2,7}$); 4.80 m, 2 H (H$_{4,5}$); 3.78 m, 2 H (H$_{3,6}$). ^{13}C{^{1}H} NMR (toluene-d_8): 1.0 (Me$_3$Si); 71.93 (C$_{2,7}$);

75.36 ($C_{3,6}$); 77.12 ($C_{8,9}$); 94.42 ($C_{4,5}$); 175.82 (C=O); 227.83, 232.40 (M-CO). For $C_{18}H_{24}O_4Si_2W$ (554.2) calculated: 39.72% C, 4.44% H; found: 39.56% C, 4.28% H.

(η^4,η^2-8,9-Diethylbicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonylmetals(0)

A solution of **2a–2c** [0.5 g: **2a** (2.06 mmol), **2b** (1.75 mmol), **2c** (1.34 mmol)] and 3-hexyne (0.280 ml, 2.29 mmol) in toluene (150 ml) was irradiated with UV light at 263 K for 820, 780 and 710 min, respectively, with a slow purge of carbon monoxide. Filtration through Celite, removal of the solvent *in vacuo*, and chromotography of the residue on alumina, eluting with pentane–dichloromethane (5 : 1) gave the reddish brown solution. The eluate was collected and evaporated *in vacuo*. The resulting residue was then recrystallized from pentane by cooling at –78 °C overnight. Decantation of the solvent drying the residue *in vacuo* produced the dark red crystals which were collected and stored under nitrogen.

(η^4,η^2-8,9-Diethylbicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonylchromium(0) (**5a**). Yield 0.4 g (60% relative to **2a**). Red solid, m.p. 152 °C. M.w.: 324 (MS). IR (hexane): ν(CO) 1972 vs, 1936 vs, 1723 s, 1582 m. ^{1}H NMR (CDCl$_3$): 1.07 t (CH$_2$Me); 2.56 m, 4 H (CH$_2$); 5.07 m, 2 H (H$_{2,7}$); 4.76 m, 2 H (H$_{4,5}$); 4.23 m, 2 H (H$_{3,6}$). ^{13}C{^{1}H} NMR (toluene-d_8): 14.30 (CH$_3$); 24.66 (CH$_2$); 68.69 (C$_{2,7}$); 78.14 (C$_{3,6}$); 84.35 (C$_{8,9}$); 97.26 (C$_{4,5}$); 175.72 (C=O); 226.40, 230.32 (M-CO). For $C_{16}H_{16}CrO_4$ (324.3) calculated: 59.26% C, 4.93% H; found: 59.48% C, 4.73% H.

(η^4,η^2-8,9-Diethylbicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonylmolybdenum(0) (**5b**). Yield 0.4 g (62% relative to **2b**). Red solid, m.p. 149 °C. M.w.: 368 (MS). IR (hexane): ν(CO) 1975 vs, 1935 vs, 1721 s, 1579 m. ^{1}H NMR (CDCl$_3$): 1.08 t (CH$_2$Me); 2.58 m, 4 H (CH$_2$); 5.16 m, 2 H (H$_{2,7}$); 4.73 m, 2 H (H$_{4,5}$); 4.26 m, 2 H (H$_{3,6}$). ^{13}C{^{1}H} NMR (toluene-d_8): 14.36 (CH$_3$); 24.75 (CH$_2$); 68.87 (C$_{2,7}$); 78.21 (C$_{3,6}$); 84.47 (C$_{8,9}$); 97.38 (C$_{4,5}$); 175.80 (C=O); 226.97, 231.12 (M-CO). For $C_{16}H_{16}MoO_4$ (368.2) calculated: 52.17% C, 4.35% H; found: 52.36% C, 4.21% H.

(η^4,η^2-8,9-Diethylbicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonyltungsten(0) (**5c**). Yield 0.4 g (65% relative to **2c**). Red solid, m.p. 148 °C. M.w.: 456 (MS). IR (hexane): ν(CO) 1973 vs, 1940 vs, 1725 s, 1585 m. ^{1}H NMR (CDCl$_3$): 1.06 t (CH$_2$Me); 2.54 m, 4 H (CH$_2$); 5.19 m, 2 H (H$_{2,7}$); 4.76 m, 2 H (H$_{4,5}$); 4.29 m, 2 H (H$_{3,6}$). ^{13}C{^{1}H} NMR (toluene-d_8): 14.32 (CH$_3$); 24.82 (CH$_2$); 68.82 (C$_{2,7}$); 78.16 (C$_{3,6}$); 84.39 (C$_{8,9}$); 97.25 (C$_{4,5}$); 175.76 (C=O); 227.59, 231.64 (M-CO). For $C_{16}H_{16}O_4W$ (456.2) calculated: 42.13% C, 3.53% H; found: 42.38% C, 3.42% H.

(η^4,η^2-8-Phenyl-9-(trimethylsilyl)bicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonylmetals(0)

A solution of **2a–2c** [0.5 g: **2a** (2.06 mmol), **2b** (1.75 mmol), **2c** (1.34 mmol)] and 1-phenyl-2-(trimethysilyl)acetylene (0.5 g, 2.87 mmol) in toluene (120 ml) was irradiated with UV light for 560, 520 and 480 min, respectively, at 263 K with a high-pressure mercury lamp. The resulting dark solution was then filtered through Celite. Evaporation of the solvent *in vacuo* produced the dark brown residue which was then chromotographed on silica gel using hexane–dichloromethane (5 : 1) mixture. The red eluate was collected and evaporated *in vacuo*. Recrystallization of the residue from pentane at –78 °C and decantation of the solvent produced the red solid wich was then dried *in vacuo*, collected and stored under nitrogen.

(η^4,η^2-8-Phenyl-9-(trimethylsilyl)bicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonylchromium(0) (**6a**). Yield 0.6 g (70% relative to **2a**). Red solid, m.p. 133 °C. M.w.: 416 (MS). IR (hexane): ν(CO) 1969 vs, 1930 vs, 1724 s, 1582 m. ^{1}H NMR (CDCl$_3$): 0.41 s (Me$_3$Si); 4.76 d, $J = 7.2$, 1 H (H$_2$ or H$_7$); 4.98 d, $J = 7.1$, 1 H (H$_2$ or H$_7$); 4.82 m, 2 H (H$_{4,5}$); 3.87 m, 2 H (H$_{3,6}$); 7.24 m, 6 H (Ph); 7.62 m, 4 H (Ph). ^{13}C{^{1}H} NMR (toluene-d_8): 1.1 (Me$_3$Si); 70.34, 72.63

(C$_{2,7}$); 76.51, 77.13 (C$_{3,6}$); 77.83, 79.06 (C$_{8,9}$); 95.63, 95.78 (C$_{4,5}$); 128.1, 128.6, 129.3, 129.9, 130.9, 131.5 (Ph); 175.62 (C=O); 226.53, 227.97, 232.14 (M-CO). For C$_{21}$H$_{20}$CrO$_4$Si (416.5) calculated: 60.65% C, 4.84% H; found: 60.83% C, 4.92% H.

(η^4,η^2-8-Phenyl-9-(trimethylsilyl)bicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonylmolybdenum(0) (**6b**). Yield 0.5 g (62% relative to **2b**). Red solid, m.p. 131 °C. M.w.: 460 (MS). IR (hexane): ν(CO) 1970 vs, 1934 vs, 1721 s, 1584 m. ^{1}H NMR (CDCl$_3$): 0.40 s (Me$_3$Si); 4.80 d, J = 7.4, 1 H (H$_2$ or H$_7$); 5.06 d, J = 7.2, 1 H (H$_2$ or H$_7$); 4.89 m, 2 H (H$_{4,5}$); 3.92 m, 2 H (H$_{3,6}$); 7.26 m, 6 H (Ph); 7.65 m, 4 H (Ph). ^{13}C{^{1}H} NMR (toluene-d_8): 1.0 (Me$_3$Si); 70.81, 73.04 (C$_{2,7}$); 76.72, 77.42 (C$_{3,6}$); 78.12, 79.47 (C$_{8,9}$); 95.82, 96.11 (C$_{4,5}$); 128.3, 128.6, 129.1, 129.8, 130.6, 131.2 (Ph); 175.65 (C=O); 226.67, 227.93, 232.26 (M-CO). For C$_{21}$H$_{20}$MoO$_4$Si (460.4) calculated: 54.78% C, 4.38% H; found: 54.56% C, 4.30% H.

(η^4,η^2-8-Phenyl-9-(trimethylsilyl)bicyclo[4.2.1]nona-3,5,8-trien-1-one)tricarbonyltungsten(0) (**6c**). Yield 0.5 g (68% relative to **2c**). Red solid, m.p. 128 °C. M.w.: 548 (MS). IR (hexane): ν(CO) 1973 vs, 1936 vs, 1723 s, 1581 m. ^{1}H NMR (CDCl$_3$): 0.40 s (Me$_3$Si); 4.79 d, J = 7.0, 1 H (H$_2$ or H$_7$); 5.02 d, J = 7.2, 1 H (H$_2$ or H$_7$); 4.86 m, 2 H (H$_{4,5}$); 3.94 m, 2 H (H$_{3,6}$); 7.23 m, 6 H (Ph); 7.67 m, 4 H (Ph). ^{13}C{^{1}H} NMR (toluene-d_8): 1.2 (Me$_3$Si); 70.64, 72.81 (C$_{2,7}$); 76.65, 77.34 (C$_{3,6}$); 78.06, 79.31 (C$_{8,9}$); 95.71, 96.03 (C$_{4,5}$); 128.4, 128.8, 129.3, 130.1, 130.7, 131.6 (Ph); 175.64 (C=O); 226.47, 227.79, 232.26 (M-CO). For C$_{21}$H$_{20}$O$_4$SiW (548.3) calculated: 46.00% C, 3.68% H; found: 46.23% C, 3.76% H.

8,9-Diphenylbicyclo[4.2.1]nona-3,5,8-trien-1-one (**7a**)

A deep red solution of **3a** (0.2 g, 0.48 mmol) in toluene was refluxed for *ca* 15 min or until it turned pale yellow. The toluene was removed under vacuum and the colorless residue purified by TLC (silica, hexane–dichloromethane 1 : 1) to give **7a** as a colorless oil. Yield 0.1 g (73% relative to **3a**), colorless oil liquid. M.w.: 284 (MS). ^{1}H NMR (CDCl$_3$): 4.81 d, J = 7.8, 2 H (H$_{2,7}$); 5.86 m, 2 H (H$_{3,6}$); 6.12 m, 2 H (H$_{4,5}$); 7.15 m, 10 H (Ph). ^{13}C{^{1}H} NMR (toluene-d_8): 74.13 (C$_{2,7}$); 126.0 (C$_{8,9}$); 128.6 (C$_{3,6}$); 139.8 (C$_{4,5}$); 126.8, 127.6, 127.9, 130.0 (Ph); 175.51 (C=O). For C$_{21}$H$_{16}$O (284.3) calculated: 88.70% C, 5.67% H; found: 88.53% C, 5.53% H.

8,9-Bis(trimethylsilyl)bicyclo[4.2.1]nona-3,5,8-trien-1-one (**8a**)

A solution of **4a** (0.25 g, 0.61 mmol) in toluene (20 ml) was stirred with an aqueous solution (5 ml) of ammonium cerium(IV) nitrate for 5 min or until it turned pale yellow. The toluene was removed *in vacuo* and the organic phase residue purified by TLC (silica, hexane–dichloromethane 1 : 1) to give **8a** as a colorless oil. Yield 0.1 g (59% relative to **4a**). M.w.: 276 (MS). ^{1}H NMR (CDCl$_3$): 4.85 d, J = 7.8, 2 H (H$_{2,7}$); 5.81 m, 2 H (H$_{3,6}$); 6.05 m, 2 H (H$_{4,5}$); 0.19 s, 18 H (Me$_3$Si). ^{13}C{^{1}H} NMR (toluene-d_8): 74.83 (C$_{2,7}$); 124.2 (C$_{8,9}$); 127.9 (C$_{3,6}$); 138.3 (C$_{4,5}$); 175.24 (C=O). For C$_{15}$H$_{24}$OSi$_2$ (276.5) calculated: 65.15% C, 8.74% H; found: 65.02% C, 8.61% H.

8,9-Diethylbicyclo[4.2.1]nona-3,5,8-trien-1-one (**9a**)

A reddish brown solution of **5a** (0.2 g, 0.62 mmol) in toluene was refluxed for *ca* 25 min or until it turned pale yellow. The toluene was removed under vacuum and the colorless residue purified by TLC (silica, pentane–dichloromethane 2 : 1) to give **9a** as a colorless oil. Yield 0.1 g (85% relative to **5a**). M.w.: 188 (MS). ^{1}H NMR (CDCl$_3$): 0.98 t, J = 7.9, 6 H (CH$_3$CH$_2$); 2.38 m, 4 H (CH$_2$Me); 4.87 m, 2 H (H$_{2,7}$); 5.97 m, 2 H (H$_{3,6}$); 6.24 m, 2 H (H$_{4,5}$).

$^{13}C\{^1H\}$ NMR (toluene-d_8): 14.75 (CH$_3$); 23.27 (CH$_2$); 70.53 (C$_{2,7}$); 137.60 (C$_{8,9}$); 124.42 (C$_{3,6}$); 146.25 (C$_{4,5}$); 175.74 (C=O). For C$_{13}$H$_{16}$O (188.3) calculated: 82.94% C, 8.57% H; found: 82.73% C, 8.71% H.

8-Phenyl-9-(trimethylsilyl)bicyclo[4.2.1]nona-3,5,8-trien-1-one (**10a**)

A solution of **6a** (0.20 g, 0.48 mmol) in toluene (20 ml) was stirred with an aqueous solution (5 ml) of ammonium cerium(IV) nitrate for 15 min or until it turned pale yellow. The toluene was removed *in vacuo* and the organic phase residue purified by TLC (silica, hexane–dichloromethane 2 : 1) to give **10a** as a colorless oil. Yield 0.1 g (74% relative to **6a**). M.w.: 280 (MS). ^1H NMR (CDCl$_3$): 4.93 d, *J* = 7.6, 2 H (H$_{2,7}$); 5.87 m, 2 H (H$_{3,6}$); 6.11 m, 2 H (H$_{4,5}$); 0.24 s, 18 H (Me$_3$Si); 7.18 m, 10 H (Ph). $^{13}C\{^1H\}$ NMR (toluene-d_8): 74.52 (C$_{2,7}$); 125.3 (C$_{8,9}$); 128.1 (C$_{3,6}$); 138.9 (C$_{4,5}$); 127.2, 128.1, 128.7, 131.4 (Ph); 175.14 (C=O). For C$_{18}$H$_{20}$OSi (280.4) calculated: 77.10% C, 7.19% H; found: 77.26% C, 7.28% H.

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