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Cationic η^3-butadienyl complexes of chromium and manganese

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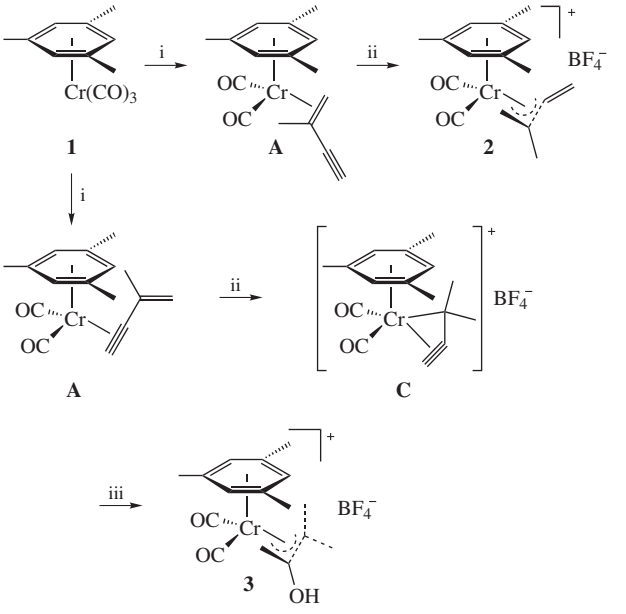
The title complexes have been synthesized by reactions of $AreneCr(CO)_3$ or $CpMn(CO)_3$ with enynes or allenylcarbinol; the stereochemistry and reactivity of these complexes have been studied.

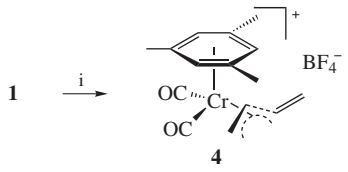
Transition metal complexes containing η^3-bonded butadienyl ligands are important because of their relationship to metal-coordinated η^3-allyls and η^2-allenes and their relevance to organic synthesis.[1] In contrast to η^3-allyl complexes, η^3-butadienyl complexes are rare and their reaction chemistry is largely unexplored. Following the discovery of the first complex containing a (1,2,3-η^3)-*trans*-butadienyl ligand by Nesmeyanov *et al*.[2] over 20 years ago, several synthetic routes to this class of complex have been established. These include an attack by metal carbonylate anions on allenes, alkynes or dienes,[3] deprotonation or desilylation of butadienes,[4] ring opening in cycloalkenyl ligands[5] and vinylidene coupling reactions.[6] As a result, complexes of Mo, W, Re, Co, Rh, Fe, Ru, Pd and Pt were prepared. These complexes are mainly neutral, except for cationic derivatives of Pd[5(*a*)] and Pt.[5(*a*),7]

This study deals with the development of methods for synthesising η^3-butadienyl complexes of Cr and Mn using enynes and allenyl carbinol as organic substrates. To this end, we used the approach developed previously[8] for the synthesis of cationic allyl complexes of metals based on UV irradiation of a mixture of a carbonyl complex with an allyl alcohol or 1,3-diene in the presence of a strong acid (HBF_4). It was found that the reaction of mesitylenechromiumtricarbonyl **1** with isopropenylacetylene under the same conditions gave a cationic mesitylenechromium-dicarbonyl complex with η^3-2-methylbutadienyl ligand **2** in high yield. It is believed that this product is formed by chromium coordination at the double bond of isopropenylacetylene (**A**) followed by protonation at the terminal carbon of the ethynyl group. In this case, one could have also expected that the product of coordination at the triple bond (**B**) would be formed; protonation of the latter should give the corresponding η^3-propargyl complex (**C**). However, as we have shown previously, such chromium derivatives are unstable and can give stable products in reactions with certain nucleophiles.[8,9] In fact, the reaction in the presence of 48% aqueous HBF_4 resulted in a mixture (19:1) of compound **2** and complex **3** with the 1,1-dimethyl-2-hydroxyallyl ligand, which is formed due to the addition of a water molecule to the intermediate propargyl complex (**C**) (Scheme 1).



Scheme 1 *Reagents and conditions*: i, $HC{\equiv}C{-}C(Me){=}CH_2$, diethyl ether, UV irradiation, room temperature; ii, $HBF_4{\cdot}OEt_2$; iii, 48% HBF_4.

The reaction involving vinylacetylene also gave cationic complex **4** with non-substituted η^3-butadienyl ligand. The same result was achieved when allenyl carbinol was used instead of a enyne (Scheme 2).



Scheme 2 *Reagents and conditions*: i, $HC{\equiv}C{-}CH{=}CH_2$ or $H_2C{=}C{=}C{-}CH_2OH$, diethyl ether, $HBF_4{\cdot}OEt_2$, UV irradiation, room temperature.

The structures of compounds **2**–**4** were studied using IR and ^1H NMR spectroscopy; in addition, a ^{13}C NMR spectrum was recorded for compound **2**[†] and single-crystall X-ray structural analysis of **4** was carried out (Figure 1).[‡] The stretching vibration frequencies ν_{CO} and chemical shifts δ for $C(1)H_2$ in the ^1H and ^{13}C NMR spectra are similar to those in chromium η^3-allyl complexes.[8] On the other hand, the values of δ for $C(4)H_2$ and C(3) in ^1H and ^{13}C NMR spectra are in the region characteristic of η^2-coordinated allene ligands. The C(1)–C(2)–C(3) and C(2)–C(3)–C(4) angles are also in the ranges typical of allyl and allene ligands, respectively.

Thus, a specific feature of the η^3-butadienyl ligand is that it is a superposition of the allyl and allene ligands. Note that complexes **2** and **3** are formed only as *endo* isomers due to the substituent at the 2-position, which is more bulky than a hydrogen atom,[8,10] whereas complex **4** is an *exo* isomer.[8,11]

Unlike compound **4**, the protonation of a mixture of isomeric complexes with allenyl carbinol **6** obtained from $CpMn(CO)_3$ **5** resulted in a mixture of *exo*:*endo* isomers **7a**:**7b** (7:1 ratio) in 30% yield (Scheme 3). The ratio of intermediate isomers

6a:**6b**:**6c** was 75:11:14. A special experiment has shown that only protonation of compound **6a** results in η^3-butadienyl complexes **7a**,**b**, whereas the treatment of **6b** and **6c** with $HBF_4{\cdot}OEt_2$ affords decomposition products.

The reactivity of η^3-butadienyl complexes has almost not been studied. EHMO analysis of the complex of Mo with the η^3-butadienyl ligand $Mo(OCOCF_3)(CO)_2(bipy)[\eta^3\text{-}CH_2C(CONHMe)C{=}CH_2]$ has shown that a nucleophilic attack in orbital-controlled reactions should involve the C(1) atom, whereas that in charge-controlled reactions should occur at the C(3) atom.[12] Only one example of this type of nucleophilic reaction is known, *viz.*, the reaction of the isoelectronic complex $CpMo(CO)_2[\eta^3\text{-}CH_2C(CONEt_2)C{=}C(Me)Ph]$ with Et_2NH that resulted in $CpMo(CO)_2(\eta^3\text{-}Et_2NCH_2)C(CONEt_2)CH{=}C(Me)Ph$ with an allyl ligand due to conjugate addition of Et_2N at the C(1) atom and H at the C(3) atom of the butadienyl ligand.[13]

Owing to their cationic nature, complexes **2**, **4** and **7** are of special interest for reactions with nucleophiles. Complex **2** smoothly reacts with the hydride ion to give derivative **8** with 1,1-dimethylallene in 80% yield. Compound **4** is also readily converted by PPh_3 to produce complex **9** with a triphenylphosphoniomethylallene ligand in 78% yield. Note that the allene ligand in both compounds **8** and **9** is coordinated at the terminal double bond. On the other hand, manganese complex **10** obtained in a similar reaction of a mixture of **7a**,**b** with PPh_3 is a different isomer with coordination on the internal double bond of the allene ligand (Scheme 4).

† All new complexes exhibited satisfactory elemental analysis data. IR spectra were measured on a Specord 75 IR spectrophotometer. ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Gemini-300 instrument at 23 °C. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual protons or ^{13}C resonances of the deuterated solvent (see Online Supplementary Materials).

For **2**: ^{1}H NMR ([$^2H_6$]acetone) δ: 6.80 (d, 1H, $=CH_a$, J_{ab} 4.8 Hz), 6.40 (s, 3H, H_{Ar}), 6.09 (d, 1H, $=CH_b$, J_{ba} 4.8 Hz), 3.80 (s, 1H, H_{syn}), 3.14 (br. s, 1H, H_{anti}), 2.32 (s, 9H, Me_{Ar}), 1.49 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ([$^2H_6$]acetone, 75.5 MHz) δ: 237.4 (br. s, CO), 179.2 (s, =C=), 120.3 (s, $C_{Ar}Me$), 110.8 (s, $=CH_2$), 107.3 (s, $C_{Ar}H$), 83.3 (s, $C_{All}Me$), 58.7 (s, $CH_{2(All)}$), 22.1 (s, Me_{All}), 19.2 (s, Me_{Ar}). IR (CH_2Cl_2, ν/cm^{-1}): 2012 (vs, ν_{CO}), 1974 (vs, ν_{CO}).

For **3**: ^{1}H NMR ([$^2H_6$]acetone) δ: 6.36 (s, 3H, H_{Ar}), 5.12 (br. s, OH), 3.85 (s, 1H, H_{syn}), 2.64 (s, 1H, H_{anti}), 2.38 (s, 9H, Me_{Ar}), 2.18 (s, 3H, Me_{syn}), 0.86 (s, 3H, Me_{anti}). IR (CH_2Cl_2, ν/cm^{-1}): 1976 (vs, ν_{CO}), 1930 (vs, ν_{CO}).

For **4**: ^{1}H NMR ([$^2H_6$]acetone) δ: 6.76 (dd, 1H, $=CH_a$, J_{ab} 5.0 Hz, ^4J 2.9 Hz), 6.60 (s, 3H, H_{Ar}), 6.15 (dd, 1H, $=CH_b$, J_{ba} 5.0 Hz, ^4J 2.9 Hz), 4.51 (ddt, 1H, H_{centr}, $^3J_1$ 11.3 Hz, $^3J_2$ 8.3 Hz, ^4J 2.9 Hz), 3.98 (d, 1H, H_{syn}, ^3J 9.0 Hz), 2.44 (s, 9H, Me_{Ar}), 1.73 (d, 1H, H_{anti}, ^3J 11.4 Hz). IR (CH_2Cl_2, ν/cm^{-1}): 1996 (vs, ν_{CO}), 1947 (vs, ν_{CO}).

For **7a**: ^{1}H NMR ([$^2H_3$]$MeNO_2$) δ: 6.79 (d, 1H, $=CH_a$, J_{ab} 6.6 Hz), 6.04 (d, 1H, $=CH_b$, J_{ba} 6.6 Hz), 5.66 (s, 5H, Cp), 5.19 (m, 1H, H_{centr}), 4.41 (d, 1H, H_{syn}, ^3J 7.4 Hz), 2.555 (d, 1H, H_{anti}, ^3J 12.2 Hz). IR ($MeNO_2$, ν/cm^{-1}): 2048 (vs, ν_{CO}), 2004 (vs, ν_{CO}).

For **7b**: ^{1}H NMR ([$^2H_3$]$MeNO_2$) δ: 6.69 (d, 1H, $=CH_a$, J_{ab} 6 Hz), 5.82 (d, 1H, $=CH_b$, J_{ba} 6 Hz), 5.61 (s, 5H, Cp), 4.71 (d, 1H, H_{syn}, ^3J 7 Hz), 3.68 (d, 1H, H_{anti}, ^3J 12 Hz).

For **8**: ^{1}H NMR (C_6D_6) δ: 4.44 (s, 3H, H_{Ar}), 2.39 (t, 3H, =CMe*Me*, ^5J 1.7 Hz), 2.29 (t, 3H, =C*Me*Me, ^5J 2.2 Hz), 1.72 (s, 9H, Me_{Ar}), 1.35 (sept., 2H, $=CH_2$, ^5J 1.9 Hz).

For **9**: ^{1}H NMR (CD_2Cl_2) δ: 7.57–7.58 (m, 15H, Ph), 5.51 (m, 1H, =CH), 5.12 (s, 3H, H_{Ar}), 4.28 (dd, 2H, CH_2, $^3J_{HH}$ 7.0 Hz, $^3J_{HP}$ 12.8 Hz), 2.01 (s, 9H, Me), 0.67 (dd, 2H, $=CH_2$, $^4J_{HH}$ 2.7 Hz, $^5J_{HP}$ 5.8 Hz). IR (CH_2Cl_2, ν/cm^{-1}): 1920 (vs, ν_{CO}), 1860 (vs, ν_{CO}).

For **10**: ^{1}H NMR (CD_2Cl_2) δ: 7.74–8.08 (m, 15H, Ph), 5.48 (br. dd, 1H, =CH*H*), 5.09 (dd, 1H, =C*H*H, $^2J_{HH}$ ~ $^4J_{HP}$ ~ 2.5 Hz), 4.94 (s, 5H, Cp), 4.59 (ddd, 1H, C*H*H), 3.21 (ddd, 1H, =CH, $^3J_{HH}$ ~ 2 Hz, $^2J_{HH}$ 15.2 Hz, $^2J_{HP}$ 12.9 Hz), 3.21 (ddd, 1H, CH*H*, $^3J_{HH}$ 9.2 Hz, $^2J_{HH}$ 15.2 Hz, $^2J_{HP}$ 12.9 Hz), 2.70 (m, 1H, =CH, $^4J_{HH}$ 2.5 Hz, $^3J_{HH}$ 8.6 Hz). IR ($MeNO_2$, ν/cm^{-1}): 1986 (vs, ν_{CO}), 1924 (vs, ν_{CO}).

‡ *Crystallographic data*. Crystals of **4** ($C_{15}H_{17}BCrF_4O_2$, M = 368.10) are monoclinic, space group $P2_1$, at 100 K: a = 9.4556(8), b = 13.6133(12) and c = 12.1874(10) Å, β = 92.156(2)°, V = 1567.7(2) Å^3, Z = 4 (Z' = 2), d_{calc} = 1.560 g cm^{-3}, μ(MoKα) = 7.76 cm^{-1}, F(000) = 752. Intensities of 11610 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71073 Å, ω-scans, $2\theta < 56°$] and 7315 independent reflections (R_{int} = 0.0276) were used in a further refinement. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The H(C) atom positions were calculated and refined in an isotropic approximation in riding model with U_{iso}(H) parameters of $1.2\,U_{eq}(C_i)$ for CH and CH_2 groups and $1.5\,U_{eq}(C_{ii})$, where $U(C_i)$ and $U(C_{ii})$ are the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bonded. For **4**, the refinement converged to wR_2 = = 0.0851 and GOF = 1.007 for all independent reflections [R_1 = 0.0385 was calculated against F for 6392 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0. The crystal contains two independent molecules in the unit cell. In one of them, the allene ligand and the carbonyl group are disordered over two sites with occupancies of 0.75:0.25.

CCDC 757986 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.

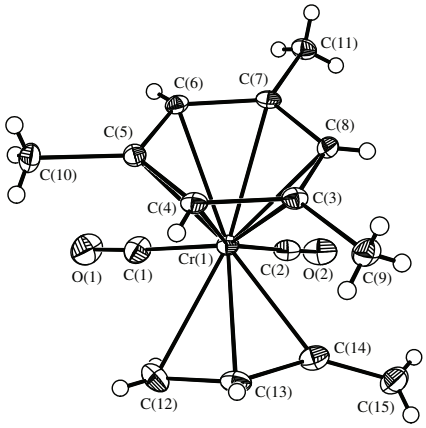
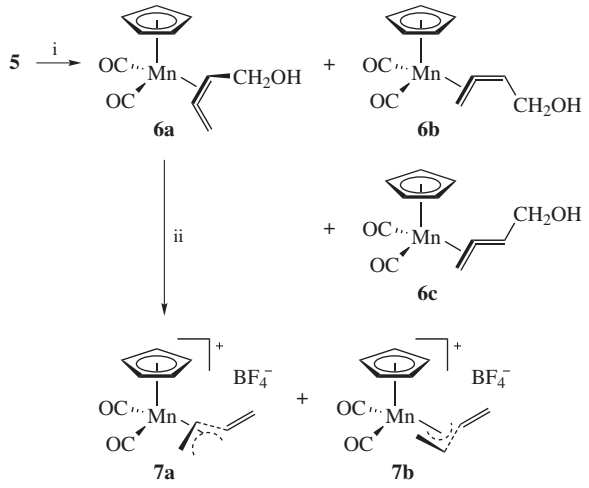
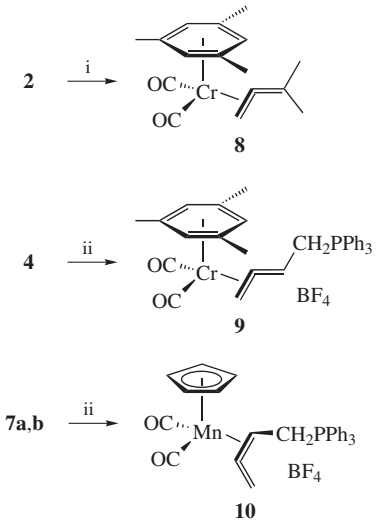


Figure 1 General view of molecule **4**. Thermal ellipsoids are drawn for the probability p = 30%. Selected bond lengths (for the ordered molecule, see experimental part for details) (Å): Cr(1)–C(1) 1.864(3), Cr(1)–C(2) 1.836(3), Cr(1)–C(12) 2.276(3), Cr(1)–C(13) 2.146(3), Cr(1)–C(14) 2.142(3), Cr(1)–C(15) 3.264(2), Cr(1)–C(3) 2.312(2), Cr(1)–C(4) 2.284(3), Cr(1)–C(5) 2.270(3), Cr(1)–C(6) 2.260(3), Cr(1)–C(7) 2.285(3), Cr(1)–C(8) 2.249(3), C(12)–C(13) 1.382(4), C(13)–C(14) 1.402(4), C(14)–C(15) 1.299(4); bond angles (°): C(2)–Cr(1)–C(1) 81.6(1), O(1)–C(1)–Cr(1) 177.3(3), O(2)–C(2)–Cr(1) 178.7(3), C(12)–C(13)–C(14) 120.3(3), C(13)–C(14)–C(15) 145.8(3).



Scheme 3 *Reagents and conditions*: i, THF, UV irradiation, ≤ 10 °C, then $H_2C{=}C{=}CH{-}CH_2OH$, room temperature; ii, $HBF_4{\cdot}OEt_2$, diethyl ether.



Scheme 4 *Reagents and conditions*: i, $NaBH_4/H_2O–Et_2O$, room temperature; ii, PPh_3.

This difference in the behaviour of chromium and manganese complexes with allene ligands can be explained by a higher bonding strength of alkene and allene ligands with the $CpMn(CO)_2$ moiety in comparison with $AreneCr(CO)_2$. For example, all three isomers of $CpMn(CO)_2(H_2C=C=CHOMe)$ were isolated in individual state,[14] whereas complexes of the $AreneCr(CO)_2$-(allene) type distinctly tend to undergo a metallotropic rearrangement to give either the terminal double bond of the allene ligand[15] or a double bond containing an electron-withdrawing substituent,[9] *i.e.*, towards the formation of a stronger complex. Thus, it may be considered that a nucleophilic attack always occurs on the C(1) atom of the butadienyl ligand to afford initially an allene complex with coordination of the metal atom to the internal double bond; this is the end product for manganese derivatives **10**, whereas similar chromium compounds readily undergo isomerisation to more stable compounds **8** and **9**, where the allene ligand is coordinated to the terminal double bond.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2010.05.019.

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