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Cycloheptatriene and -enyl Complexes of the Early Transition Metals

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I. Abbreviations

COD	1,5-cyclooctadiene
Cy	cyclohexyl
dippe	1,2-bis(diisopropylphosphino)ethane
dme	1,2-dimethoxyethane
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
en	ethylenediamine
Fc	ferrocene
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
MO	molecular orbital
MVS	metal vapor synthesis
PE	photoelectron
r.t.	room temperature
SCE	saturated calomel electrode
TCNE	tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane
THF	tetrahydrofuran
tmeda	*N,N,N',N'*-tetramethylethylenediamine

II. Introduction

The η-cyclopentadienyl (η^5-C_5R_5) and η-arene (η^6-C_6R_6) groups are among the most common classes of ligand encountered in organotransition metal chemistry. Transition metal complexes with these ligands have been studied extensively and many of which have contributed to the development of areas such as homogeneous catalysis,[1] organic synthesis,[2] new materials,[3] and biological and medical sciences.[4] Although cycloheptatriene (η^6-C_7H_8) and cycloheptatrienyl (η^7-C_7H_7) transition metal complexes have been known for over three decades, surprisingly, the chemistry of these ligands has been studied little in comparison with that of cyclopentadienyl and arene ligands.

The first η^6-cycloheptatriene complex, Mo(η^6-C_7H_8)(CO)$_3$, was prepared by Wilkinson *et al.* in 1958,[5] and the first η^7-cycloheptatrienyl complex, [Mo(η^7-C_7H_7)(CO)$_3$][BF$_4$], was synthesized shortly after.[6] The early developments of the chemistry of η-C_7-ring transition metal compounds has been reviewed by Deganello, up to the late 1970s.[7] At that time, cycloheptatriene and -enyl complexes of the group 4 and 5 metals were rare and confined mainly as the sandwich complexes M(η^7-C_7H_7)(η^5-C_5H_5) (M = Ti, Zr, V, or Nb), M(η^7-C_7H_7)(η^5-C_7H_9) (M = Ti or V), V(η^6-C_7H_8)$_2$, and [V(η^7-C_7H_7)$_2$]$^{2+}$, and the metal carbonyl V(η^7-C_7H_7)(CO)$_3$. For the group 6 metals, in particular, molybdenum, ready accessibility of several precursors, such as M(η^6-C_7H_8)(CO)$_3$ (M = Cr, Mo, or W), [M(η^7-C_7H_7)(CO)$_3$]$^+$ (M = Cr, Mo, or W), M(η^7-C_7H_7)(CO)$_2$X (M = Mo or W; X = halides), and [Mo(η^7-C_7H_7)(η^6-C_6H_5Me)]$^+$, led to a wider range of complexes.

During the past decade more convenient synthetic pathways to several key compounds have been developed; more compounds have been synthesized and structurally characterized and a deeper understanding on the bonding of η^7-cycloheptatrienyl transition metal complexes has been realized with the aid of photoelectron spectroscopy. The purpose of this review is to provide an overview of the current status in this field of research and to stimulate further research.

In this article, only η^6-cycloheptatriene and η^7-cycloheptatrienyl complexes of the group 4, 5, and 6

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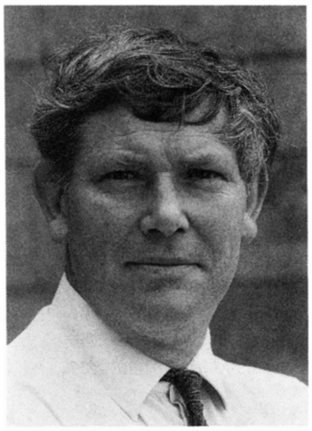
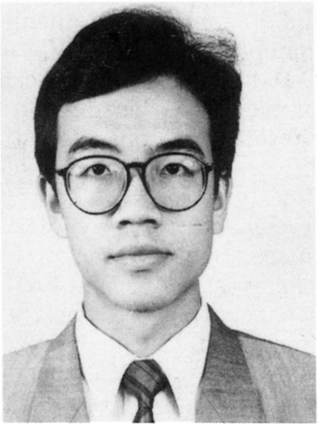


Malcolm L. H. Green obtained his Ph.D. at Imperial College of Science and Technology in 1959 (with Geoffrey Wilkinson). He moved to Cambridge as a Demonstrator in 1960 and a Fellow of Corpus Christi College in 1961. He was appointed Fellow and Tutor in Inorganic Chemistry at Balliol College, Oxford, in 1963, and became Professor of Inorganic Chemistry at Oxford University in 1989. He has been an A. P. Sloan Visiting Professor at Harvard University (1973) and a Sherman Fairchild Visiting Scholar at the California Institute of Technology (1981). His work has been recognized by the award of a Corday-Morgan Medal, a Tilden Lectureship and Prize, and the ACS Award for Inorganic Chemistry (1984) and he was elected Fellow of the Royal Society in 1985. He has published two books and over 400 articles in the field of organotransition metal chemistry.



Dennis K. P. Ng was born in Hong Kong in 1965. He received his B.Sc. with First Class Honors from The Chinese University of Hong Kong in 1988 and his M.Phil. from the same institution in 1990 under the guidance of Tien-Yau Luh. During this time, he also carried out research at the Chemistry Department of National Taiwan University (September–December, 1988). His doctoral training was at Balliol College, Oxford University, where he studied the chemistry of cycloheptatrienyl derivatives of group 6 metals under the direction of Malcolm L. H. Green and received his D.Phil. in 1993. He was the recipient of a Croucher Foundation Studentship (1988–1990) and Scholarship (1990–1993). He became a Research Fellow in Chemistry at the California Institute of Technology working with Seth R. Marder (1993–1994). In September 1994 he was appointed as a Lecturer in Chemistry at The Chinese University of Hong Kong. His current research interests are centered on bioinorganic chemistry and metallophthalocyanine chemistry.

transition metals will be reviewed. For the late transition metals, complexes with lower hapticity are dominant and will not be covered. Complexes with cycloheptatriene derivatives such as tropone, heptafulvene, azulene, heptalene, and sesquifulvalene will also be excluded. This review covers work published from 1980 up to mid-1994. Only a selection of the work described in the earlier review[7] is included in this article.

III. Synthetic Methods

Synthetic routes to η^6-cycloheptatriene and η^7-cycloheptatrienyl metal complexes can be broadly classified according to the class of starting material, namely, from metal carbonyls, from metal atoms, and from metal chlorides. Specialty and unique routes are presented at the end of this section.

A. From Metal Carbonyls

A traditional method for the preparation of cycloheptatriene complexes involves the displacement of carbonyl groups of homoleptic metal hexacarbonyls by a cycloheptatriene ligand giving $M(\eta^6\text{-}C_7H_8)(CO)_3$, where M = Cr, Mo, or W. This method works very well for chromium and molybdenum,[5,8] but for tungsten, it is much more convenient to first prepare the tris(alkanenitrile)s $W(RCN)_3(CO)_3$ (R = Me,[9] Et, or Pr[10]). The η-cycloheptatriene complexes undergo hydride abstraction readily giving the corresponding η-cycloheptatrienyl complexes (Scheme 1).[6,9,11]

Recently, this method has been extended to the preparation of substituted cycloheptatriene and -enyl complexes.[12] Thus, treatment of $Mo(CO)_6$ with 1,3,5,7-tetramethylcycloheptatriene in refluxing octane gives the expected $Mo(\eta^6\text{-}C_7H_4Me_4\text{-}1,3,5,7)(CO)_3$ (**1**) together with the isomers $Mo(\eta^6\text{-}C_7H_4Me_4\text{-}1,2,4,6)(CO)_3$ (**2**) and $Mo(\eta^6\text{-}C_7H_4Me_4\text{-}1,3,4,6)(CO)_3$ (**3**). The latter two complexes arise as a result of sequential 1,5-shifts of the 7-*endo*-hydrogen atom of the initially formed **1** (see section VI.A.1). The inseparable mixture of **2** and **3**, upon treatment with Ph_3C^+, affords the cycloheptatrienyl cation $[Mo(\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6)(CO)_3]^+$ (**4**). However, the same reaction with compound **1** gives **4** in only moderate yield even under more vigorous conditions. Probably, the 7-*exo*-methyl group of **1** hinders the approach of the bulky Ph_3C^+ cation (Scheme 2).

Treatment of $V(CO)_6$ with cycloheptatriene gives the cycloheptatrienyl complex $V(\eta^7\text{-}C_7H_7)(CO)_3$ directly.[13] Several monosubstituted cycloheptatrienyl vanadium complexes $V(\eta^7\text{-}C_7H_6R)(CO)_3$ (where R = Me, Ph, CN, OMe, OPr, or CO_2Et) can also be prepared by this method.[14]

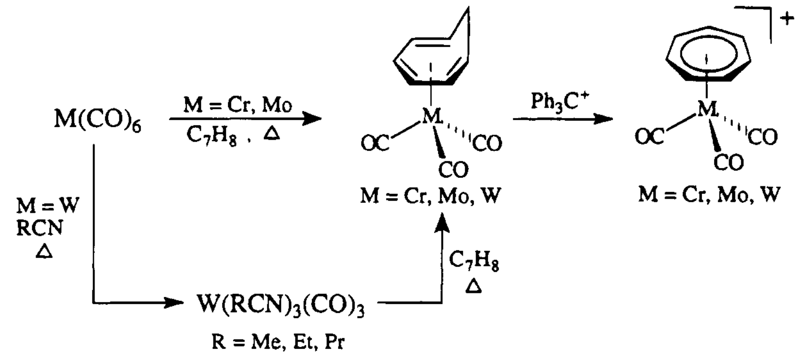
B. From Metal Atoms

Metal vapor synthesis (MVS) has been proved to be a versatile method for the preparation of low-valent metal complexes.[15] Many complexes which as yet cannot be prepared by other methods can be synthesized by means of cocondensation techniques. This method has been used to prepare the compounds $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$, where M = Ti,[16] Zr,[17] Hf,[17] V,[16] Cr,[18] Mo,[19] or W,[19] by cocondensation of the metal atoms with cycloheptatriene (Scheme 3).

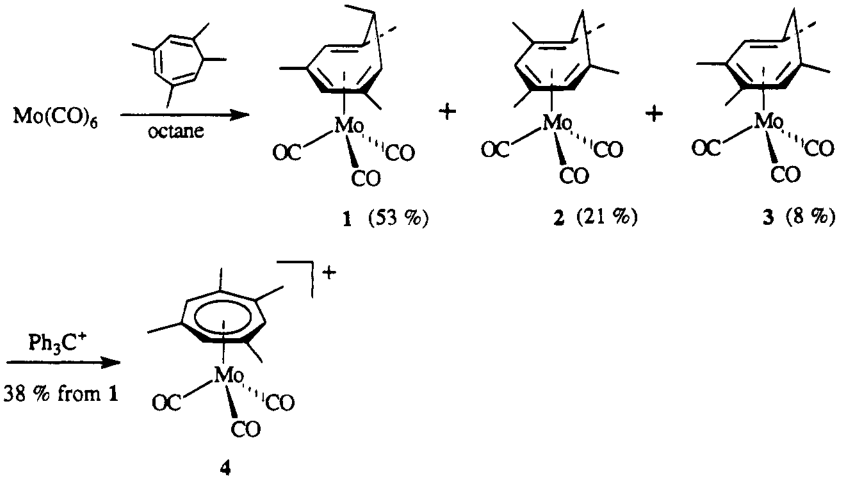
Cocondensation of zirconium or hafnium atoms with cycloheptatriene gives an ill-defined red solid with a stoichiometry close to $M(C_7H_8)_3$. Vacuum pyrolysis at 120−160 °C followed by recrystallization of the red sublimates affords pure $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$ (M = Zr or Hf) in 15−20% yield.[17]

It was reported that, when a solution of cycloheptatriene in hexane or methylcyclohexane is cocondensed with chromium vapor, the only isolable product is $Cr(\eta^7\text{-}C_7H_7)(\eta^4\text{-}C_7H_{10})$.[16,20] However, when

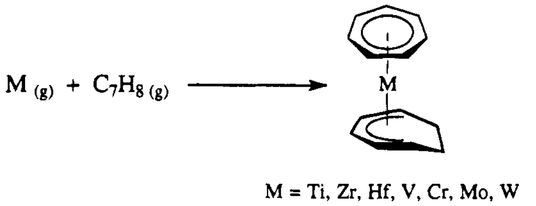
Scheme 1



Scheme 2



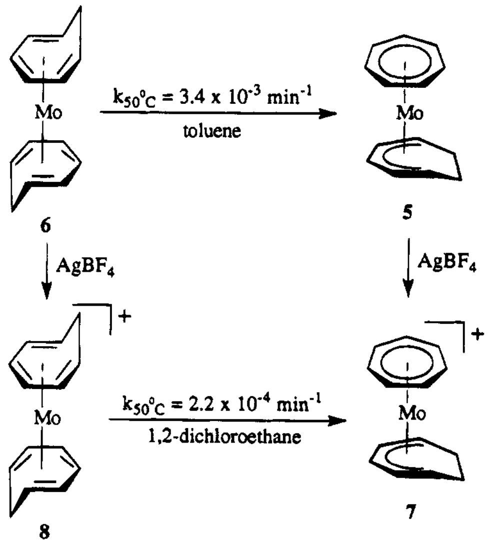
Scheme 3



neat cycloheptatriene is used, the reaction gives Cr(η^7-C_7H_7)(η^5-C_7H_9) in 45% yield with only a small amount of Cr(η^7-C_7H_7)(η^4-C_7H_{10}).[18]

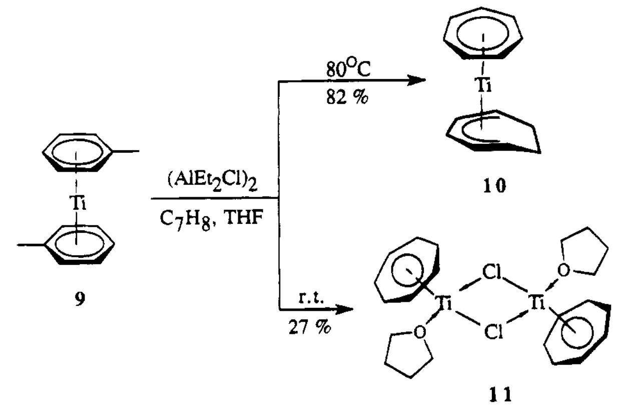
The reaction between molybdenum atoms and cycloheptatriene was originally reported by Skell *et al.* to give Mo(η^7-C_7H_7)(η^5-C_7H_9) (**5**).[19] However, a reexamination of this reaction by Green *et al.*, including a low-temperature isolation procedure, showed that the thermally sensitive bis(triene) compound Mo(η^6-C_7H_8)$_2$ (**6**) was formed in good yields. This compound proved to be unstable over long periods of time or on heating and rearranged cleanly via hydrogen migration to the more stable **5**.[21] Both **5** and **6** can be oxidized by $AgBF_4$ to give the corresponding cations [Mo(η^7-C_7H_7)(η^5-C_7H_9)]$^+$ (**7**) and [Mo(η^6-C_7H_8)$_2$]$^+$ (**8**). The latter cation **8** also rearranges to the former cation **7** but the rate is slower than their neutral analogs, as is consistent with the activation energy difference of 14 ± 3 kJ/mol (Scheme 4). Thermal rearrangement of mixtures of **6** and [D_{16}]-**6** gives only **5** and [D_{16}]-**5**; no H/D crossover could be detected by mass spectrometry. Similar results were obtained for the conversion of mixtures of **8** and [D_{16}]-**8**. These experiments together with the kinetic studies showed that the rearrangements are intramolecular.[21]

Scheme 4

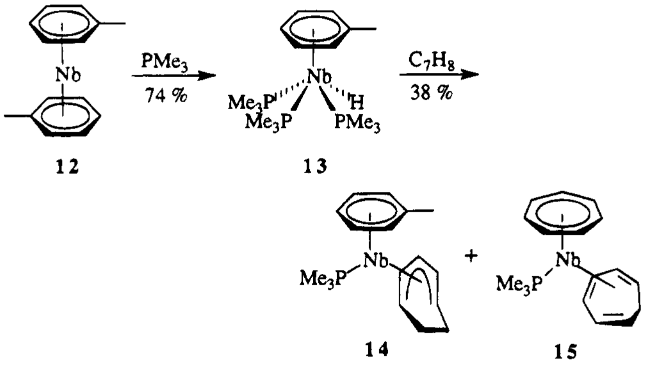


The MVS technique also provides indirect routes to cycloheptatriene and -enyl metal complexes. For example, the sandwich compound Ti(η^6-C_6H_5Me)$_2$ (**9**), which is readily available from MVS, reacts with a mixture of $(AlEt_2Cl)_2$ and a 2-fold excess of cycloheptatriene in THF at 80 °C for 2 h giving Ti(η^7-C_7H_7)(η^5-C_7H_9) (**10**) in good yield. However, when the reaction is carried out at room temperature over a period of weeks, with the minimum quantity of solvent and $(AlEt_2Cl)_2$, together with a considerable

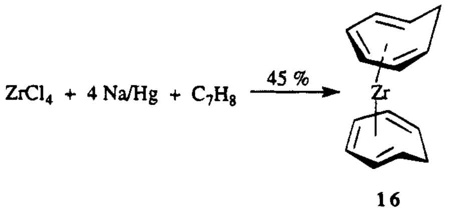
Scheme 5



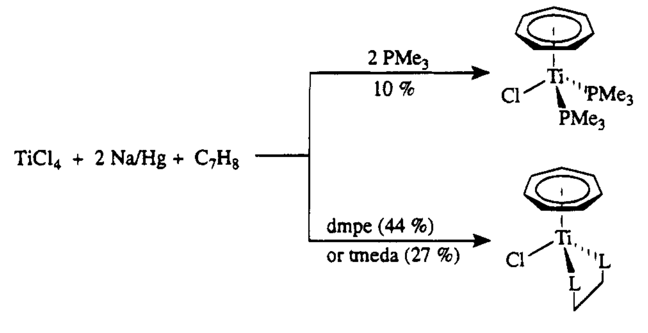
Scheme 6



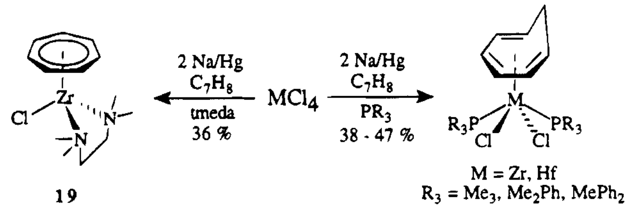
Scheme 7



Scheme 8



Scheme 9



excess of cycloheptatriene, the crystallographically characterized dimer [Ti(η^7-C$_7$H$_7$)(THF)(μ-Cl)]$_2$ (**11**) can be isolated in *ca.* 30% yield (Scheme 5). This dimer, upon treatment with an excess of cycloheptatriene and (AlEt$_2$Cl)$_2$ in THF at 80 °C, converts to **10**. Thus it appears that **11**, or a related species, such as Ti(η^7-C$_7$H$_7$)(THF)$_2$Cl, is an intermediate in the formation of **10** from **9**.[22]

As another example, the sandwich compound Nb(η^6-C$_6$H$_5$Me)$_2$ (**12**) prepared by MVS reacts with trimethylphosphine giving the half-sandwich compound Nb(η^6-C$_6$H$_5$Me)(PMe$_3$)$_3$H (**13**). Heating a solution of **13** with cycloheptatriene yields a mixture of Nb(η^6-C$_6$H$_5$Me)(η^5-C$_7$H$_9$)(PMe$_3$) (**14**) and Nb(η^7-C$_7$H$_7$)(η^4-C$_7$H$_8$)(PMe$_3$) (**15**) in 1:2 ratio (Scheme 6).[23]

C. From Metal Chlorides

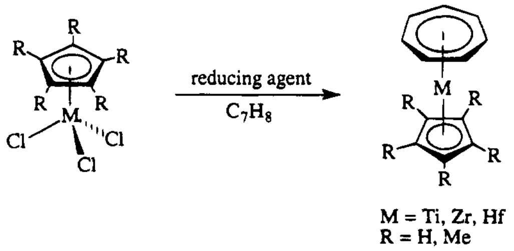
Reduction of metal halides in the presence of olefins is a commonly used method to prepare low-valent metal (π-olefin) complexes. Recently, this method has been used to prepare several key compounds which can generate a wide range of cycloheptatriene and -enyl complexes of the group 4, 5, and 6 metals. These synthetic pathways thus represent direct and convenient entries to these classes of compounds.

Reduction of ZrCl$_4$ with sodium amalgam in the presence of cycloheptatriene at <-10 °C leads to the rare formally zerovalent zirconium complex Zr(η^6-C$_7$H$_8$)$_2$ (**16**) (Scheme 7), which is a reactive precursor toward new organometallic compounds of zirconium. When this reaction is carried out at room temperature, an inseparable mixture of **16** and Zr(η^7-C$_7$H$_7$)(η^5-C$_7$H$_9$) (**17**) is formed. Similarly, reduction of TiCl$_4$ with magnesium turnings in the presence of cycloheptatriene gives a *ca.* 4:1 mixture of the bis(triene) compound Ti(η^6-C$_7$H$_8$)$_2$ (**18**) and Ti(η^7-C$_7$H$_7$)(η^5-C$_7$H$_9$) (**10**). Solutions of **18** readily decompose to **10** and it is not possible to isolate pure **18**.[24] This reaction is closely analogous to the previous route to compound **10** using isopropylmagnesium bromide as reducing agent.[25]

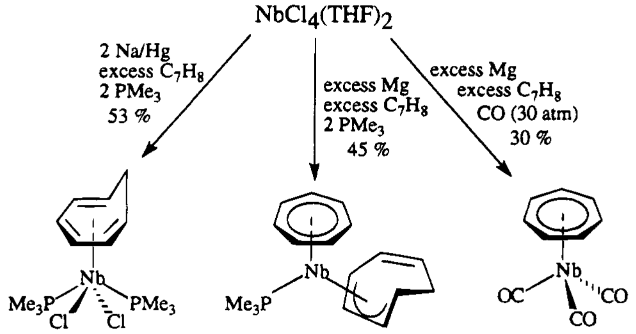
Treatment of TiCl$_4$ with 2 equiv of sodium amalgam, an excess of cycloheptatriene, and 1 equiv of L$_2$ [L$_2$ = dmpe, tmeda, or (PMe$_3$)$_2$] gives the half-sandwich compounds Ti(η^7-C$_7$H$_7$)L$_2$Cl in a one-pot reaction (Scheme 8).[26] The reaction of ZrCl$_4$ with tmeda under similar conditions generates the zirconium analog Zr(η^7-C$_7$H$_7$)(tmeda)Cl (**19**).[26] The reaction with tertiary phosphine ligands, however, gives the cycloheptatriene complexes Zr(η^6-C$_7$H$_8$)(PR$_3$)$_2$Cl$_2$ in moderate yields and these reactions can be extended to hafnium (Scheme 9).[27,28] The chemistry of divalent complexes of zirconium and hafnium is relatively unexplored. This reductive method provides a convenient way to prepare these novel compounds in multigram quantities.

The mixed-sandwich complexes M(η^7-C$_7$H$_7$)(η^5-C$_5$R$_5$) (M = Ti, Zr, or Hf; R = H or Me) can also be prepared by a reductive method. Treatment of cyclopentadienylmetal chlorides M(η^5-C$_5$R$_5$)Cl$_3$ with appropriate reducing agents, such as magnesium, aluminium, zinc, or isopropylmagnesium bromide, in the presence of cycloheptatriene gives the corresponding sandwich compounds in low (for M = Hf) to moderate (for M = Ti or Zr) yields (Scheme 10).[29-33] The reaction may be promoted with a small amount of FeCl$_3$.[34]

Scheme 10

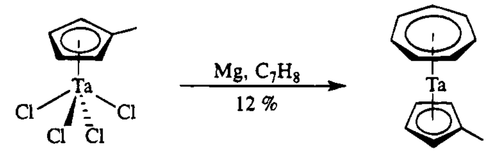


Scheme 11



20 21 22

Scheme 12

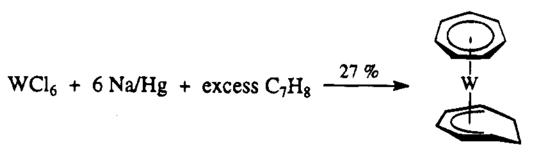


24 23

Related reactions on niobium have also been studied. The reduction of $NbCl_4(THF)_2$ with sodium amalgam or magnesium turnings in the presence of cycloheptatriene and other ligands, such as PMe_3 or CO, gives the compounds $Nb(\eta^6\text{-}C_7H_8)(PMe_3)_2Cl_2$ (**20**), $Nb(\eta^7\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)$ (**21**), or $Nb(\eta^7\text{-}C_7H_7)(CO)_3$ (**22**) in moderate yields (Scheme 11).[35] These complexes are good precursors to other $Nb(\eta^7\text{-}C_7H_7)$ derivatives. Thus these one-pot reactions provide convenient routes to the virtually unexplored $Nb(\eta^7\text{-}C_7H_7)$ system.

The sandwich complexes $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4R)$ (M = V, Nb, or Ta; R = H or Me) can be prepared by treating the corresponding η-(cyclopentadienyl)metal chlorides with magnesium or isopropylmagnesium bromide in the presence of cycloheptatriene.[36-38] For example, the first η^7-(cycloheptatrienyl)tantalum compound, namely $Ta(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)$ (**23**) has been synthesized from $Ta(\eta^5\text{-}C_5H_4Me)Cl_4$ (**24**) in 12% yield (Scheme 12).[37]

Scheme 13



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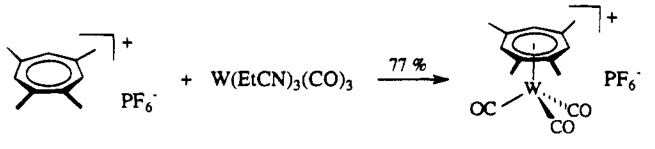
Scheme 14



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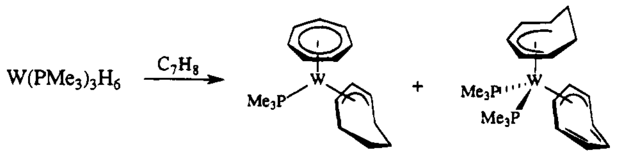
Scheme 15



27 (18 %) 28 (20 %)

Fischer *et al.* first reported the reduction of $CrCl_2$, $MoCl_5$, and WCl_6 in the presence of cycloheptatriene and cyclopentadiene (or cyclopentadienide). These reactions gave the mixed-sandwich compounds $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ (M = Cr, Mo, or W) in one-step but in very low yields (<2%).[39] An improved route to the molybdenum compound $Mo(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ (15% yield) was then reported which employs $MoCl_3(THF)_3$ as starting material.[31] Recently, the sandwich compounds $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4R)$ (M = Mo or W; R = H or Me) have been synthesized by reducing the corresponding η-cyclopentadienyl complexes $M(\eta^5\text{-}C_5H_4R)Cl_4$ with magnesium turnings or sodium amalgam in the presence of cycloheptatriene. These preparations, however, also suffer from a poor yield.[40]

Treatment of $MoCl_5$ with 5 equiv of sodium amalgam in the presence of excess cycloheptatriene affords a mixture of $Mo(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$ (**5**) and $Mo(\eta^6\text{-}C_7H_8)_2$ (**6**) in 1:1.7 ratio. Upon mild thermolysis, compound **5** can be isolated as the sole product in 39% yield.[41] Using $MoCl_4(THF)_2$ as starting material gives similar results. The tungsten compound $W(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$ (**25**) can also be prepared similarly from WCl_6 (Scheme 13).[42] However, in contrast to the corresponding molybdenum chemistry, the bis(cycloheptatriene) complex $W(\eta^6\text{-}C_7H_8)_2$ could not be isolated. Presumably the intramolecular hydrogen migration for $W(\eta^6\text{-}C_7H_8)_2$ is faster than that for **6**. The primary advantage of this method is the convenient preparation of synthetically useful compounds **5** and **25** in one pot and in gram quantities.

D. Other Methods

Nucleophilic attack on the C_7 ring in (η^7-cycloheptatrienyl)metal complexes provides an alternative entry to (η^6-cycloheptatriene)metal complexes. The details are illustrated in section VI.B.2.

In general, the reactions of tropylium cation with substitution-labile metal species do not give cycloheptatrienylmetal complexes. For example, treatment of $[C_7H_7][BF_4]$ with anion $[Mn(CO)_5]^-$ only yields the self-coupled products $Mn_2(CO)_{10}$ and $C_{14}H_{14}$.[5] Nevertheless, this method has been utilized to prepare the (1,2,4,6-tetramethylcycloheptatrienyl)tungsten complex **26** (Scheme 14).[43]

The readily available tungsten polyhydride complex $W(PMe_3)_3H_6$ can also be used to prepare cycloheptatrienyltungsten complexes. It reacts with cycloheptatriene at 80 °C giving a mixture of separable $W(\eta^7\text{-}C_7H_7)(\eta^3\text{-}C_7H_{11})(PMe_3)$ (**27**) and $W(\eta^3\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)(PMe_3)_2$ (**28**) (Scheme 15).[44]

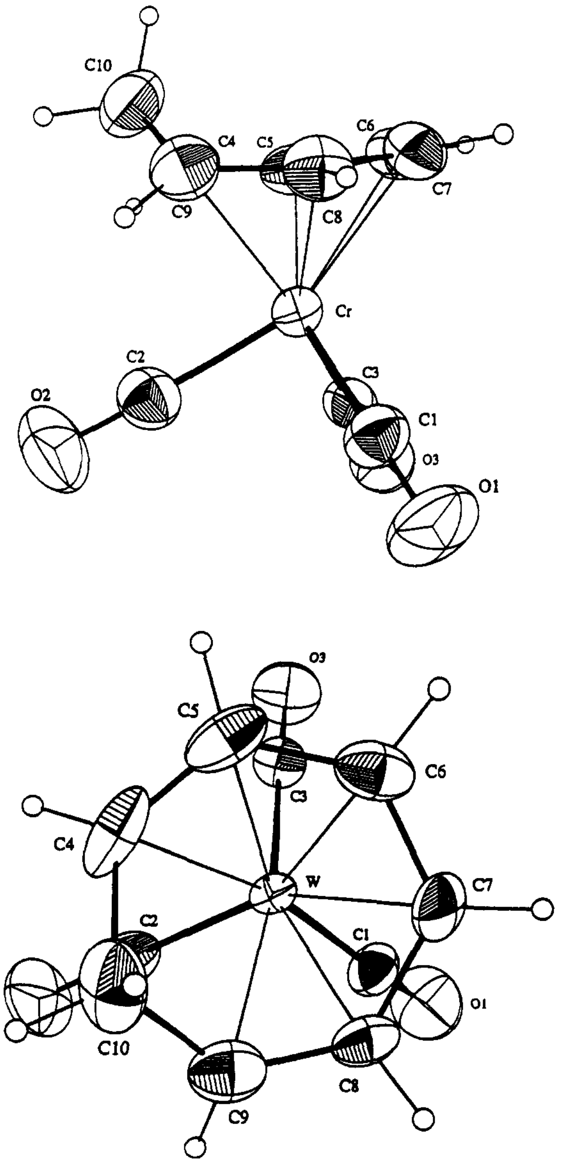


Figure 1. ORTEP drawings of (a) Cr(η^6-C_7H_8)(CO)$_3$ and (b) W(η^6-C_7H_8)(CO)$_3$.

IV. Structure

The structure of Mo(η^6-C_7H_8)(CO)$_3$ was determined in 1960.[45] This showed that the triene ring carbon atoms are approximately coplanar with alternating single and double carbon–carbon bonds. The molecule adopts a staggered structure with an approximate symmetry plane which passes through the molybdenum atom, the unique carbonyl ligand, and the methylene group. Detailed analysis of the structures of chromium and tungsten analogs has recently been performed.[46] These compounds are entirely isostructural with the molybdenum compound. However, some points mentioned in the early study appear to oversimplify the actual situation. Figure 1 shows the ORTEP drawings of Cr(η^6-C_7H_8)(CO)$_3$ and W(η^6-C_7H_8)(CO)$_3$ in different perspective views. Close examination of the chromium (and tungsten) data reveals that atoms C4/C5/C8/C9 are planar within 0.002 Å (for W, 0.01 Å), while C6 and C7 lie 0.17 Å (for W, 0.14 Å) and 0.18 Å (for W, 0.16 Å) above the plane. The obtuse angle between the C4/C5/C8/C9 and C5/C6/C7/C8 planes is 171.0° (for W, 172.4°). Thus the coordinated cycloheptatriene ring actually exists in a flattened boat conformation.

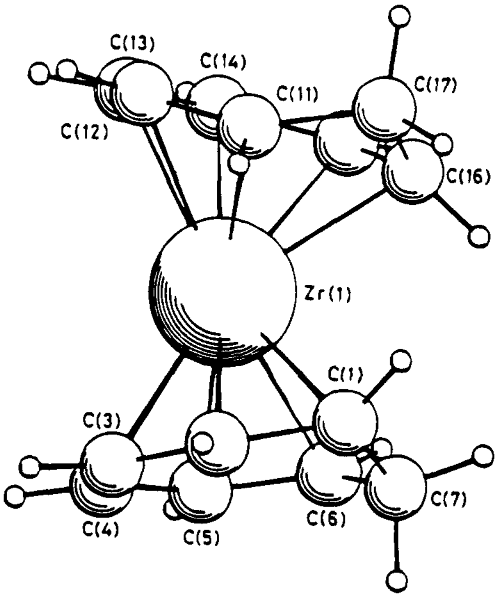


Figure 2. Molecular structure of Zr(η^6-C_7H_8)$_2$.

Close inspection of the data for M(η^6-C_7H_8)(CO)$_3$ (M = Cr, Mo, or W) also reveals that the six-membered pseudo-ring carbon–carbon bonds exhibit three different sets of values rather than two. For the Cr, Mo, and W compounds, the C4–C5 and C8–C9 bonds average 1.351 (15, 16, 6) Å, which is identical to the double-bond length in free cycloheptatriene while C5–C6 and C7–C8 bonds average 1.426 (17, 18, 6) Å, which is slightly longer than the single-bond length in free cycloheptatriene. The unusual observation is the lengthening of the C6–C7 bond, which averages 1.397 (15, 21, 3) Å. This distance is longer than the corresponding value for free cycloheptatriene and approaches the single-bond length observed in the pseudo-ring.

The other interesting observation for these structures is that the metals do not lie perpendicularly under the centroid, but shift slightly toward the C6–C7 π-bond in the pseudo-ring. This, together with the flattened boat conformation, argues that the ring may be described as η^4,η^2 -bound rather than η^6-bound, with the C6–C7 bond acting independently of the C4–C5 and C8–C9 bonds.[46]

The barriers of rotation about the cycloheptatriene–Cr axis of Cr(η^6-C_7H_7R-7)(CO)$_3$ (R = H, Me, OMe, Bu^t, or CN) have been determined by a complete line-shape analysis of the ^{13}C resonances of the carbonyl groups as a function of temperature.[47] The values of $\Delta H^{\ddagger}$ depend slightly on the substituent at the 7-position and range from 37.2 to 45.6 kJ/mol.

The structure of Zr(η^6-C_7H_8)$_2$ (**16**) has recently been determined.[24] It shows an unusual bent arrangement with a dihedral angle between the best planes of the two C_7H_8 rings of 25.6° and the methylene groups are staggered and on the same side of the molecule (Figure 2). This is in contrast to that of Mo(η^6-C_7H_8)$_2$ (**6**), which has a normal parallel arrangement of the rings with the methylene groups on opposite side of the molecule.[21b] The five C–C distances within the coordinated portion of the C_7 ring of **16** do not show alternating short and long

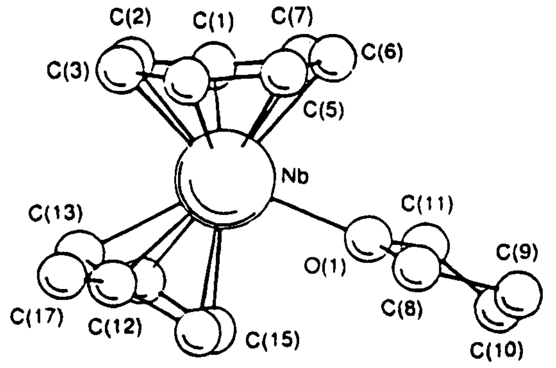


Figure 3. Molecular structure of $[Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)(THF)]^+$.

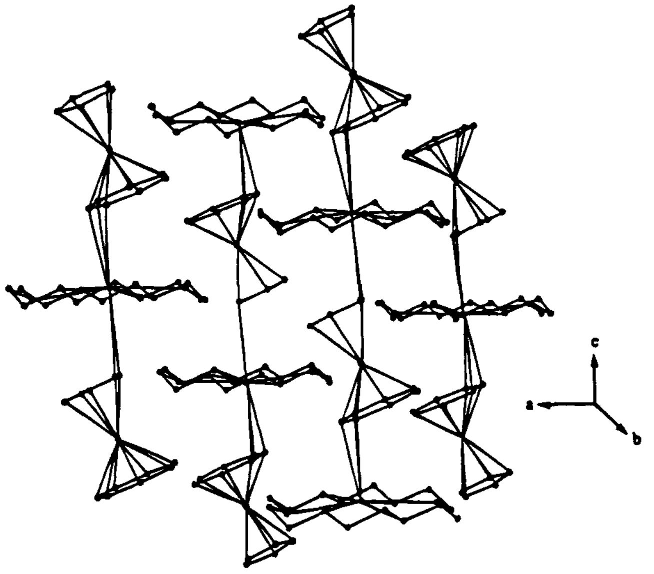


Figure 4. Crystal structure of $[K(18\text{-crown-}6)][Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$.

distances. Lack of alternation has also been found for $Nb(\eta^6\text{-}C_7H_8)(PMe_3)_2Cl_2$[35b] and $Zr(\eta^6\text{-}C_7H_7SiMe_3\text{-}7)(PMe_3)_2I_2$.[27]

The structures of (η^7-cycloheptatrienyl)metal complexes usually show a planar and regular seven-membered ring bound symmetrically to the metal center. For example, the molecular structure of $Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ in the gas phase, which has recently been determined by electron diffraction at 470 K, shows that the niobium atom is sandwiched by two parallel and symmetric rings.[48a] However, some exceptions have been reported. For example, the cycloheptatrienyl ring in $[Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)(THF)][PF_6]$ is not planar, but displays a significant "dishing" of the ring as defined by the Nb–C bond lengths (Figure 3).[37,48b] The salt $[K(18\text{-crown-}6)][Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ has an unusual crystal structure. As shown in Figure 4, the potassium ion is not equidistant from each of the carbons of a particular ring. As a result, there is a marked variation of C–C bond lengths within the C_7 ring.[37,48b]

Deviation of the C_7 ring substituents from the plane defined by the ring carbon atoms has been observed for some (η^7-cycloheptatrienyl)metal complexes. For example, the average bending of the C_7 hydrogen atoms is 10° toward the Ti atom in $Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5Me_5)$ (Figure 5).[33] The hydrogen atoms of the η^7-C_7H_7 group in $[Ti(\eta^7\text{-}C_7H_7)(THF)(\mu\text{-}Cl)]_2$ (**11**) and $Ti(\eta^7\text{-}C_7H_7)(dmpe)Et$ also have a similar out-of-plane displacement.[22] Such deviation can be attributed to a reorientation of the ring for better metal overlap.[49] It is worth mentioning that the zirconium analog $Zr(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5Me_5)$ does not show a similar bending.[50] Presumably, the larger Zr fits better than Ti and no inward bending and consequent rehybridization is necessary.

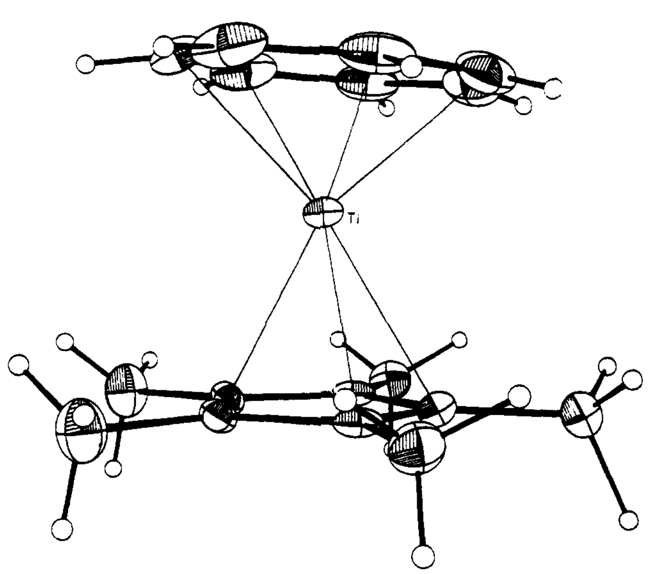


Figure 5. Molecular structure of $Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5Me_5)$.

The activation energies for ring rotation in solid $[M(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ (M = Cr or Mo) have been determined by proton spin–lattice relaxation time measurements.[51] These values are quite close (Cr, 12.8; Mo, 13.6 kJ/mol) which may reflect the fact that these complexes are isostructural with similar packing densities.

V. Bonding

The η^6-cycloheptatriene ligand can be considered as a coordinated triene and the bonding scheme for $M-(\eta^6\text{-}C_7H_8)$ is well-documented.[52] Recently, an examination of the bonding in $Zr(\eta^6\text{-}C_7H_8)_2$ (**16**) and its variation with the angle between the rings has been performed using charge-iterative extended Hückel molecular orbital calculations.[24b] The MO diagram of **16** obtained from the calculations is shown in Figure 6, which also illustrates how the frontier MO's can be derived from those of benzene. It is evident that on opening the ring linkage between C(1) and C(6) those orbitals which are bonding across C(1) and C(6) are destabilized and those which are antibonding between C(1) and C(6) are stabilized. These shifts result in the HOMO π_3 being higher in energy in cycloheptatriene than in benzene and the LUMO π_4 being lower in energy in cycloheptatriene than in benzene. Cycloheptatriene is thus set up to be both a better donor and a better acceptor than benzene. Orbital 43, the LUMO in **16**, is essentially a d_{z^2} orbital, whereas orbitals 44 and 45 are hybrid orbitals in which the $d_{x^2-y^2}$ and d_{xy} orbitals mix strongly with the two π_4 orbitals from the rings.

Studies of the effects of bending the cycloheptatriene rings have showed that orbitals 44 and 45 exhibit a stabilization in energy on bending with a minimum energy at a similar angle to that obtained

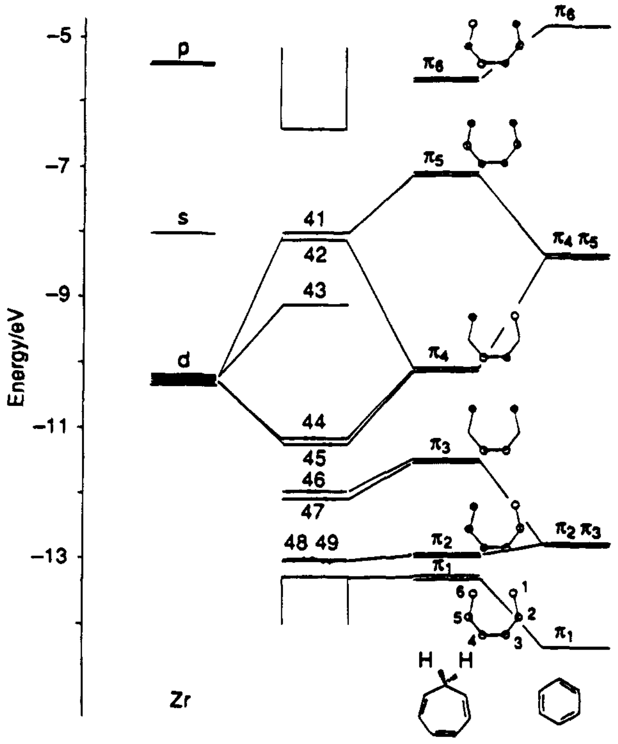
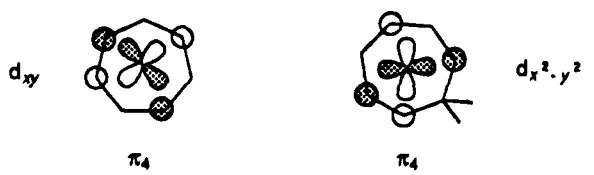


Figure 6. Qualitative molecular orbital diagram for $Zr(\eta^6\text{-}C_7H_8)_2$.

Scheme 16



from the X-ray structure, although they predict a slight destabilization in the total energy for the system. Similar stabilization has not been obtained for other orbitals in **16**.[24b]

The origin of the staggered structure in **16** has also been discussed.[24b] For an eclipsed configuration of the complex (C_{2v} symmetry), combinations of π_4 transform as b_2 and a_2, but $d_{x^2-y^2}$ and d_{xy} transform as b_2 and a_1, so only one of the d orbitals is of correct symmetry to back-donate to the ligand. If, however, the complex is staggered (C_2 symmetry) then both orbitals can back-donate as shown in Scheme 16. The geometric structure of **16** has also been predicted by ab initio MO calculations to yield a consistent interpretation of the experimental data.[53]

The bonding between the metal and η^7-cycloheptatrienyl ligand, however, has been the subject of recent debate. This ligand was originally regarded as a coordinated aromatic tropylium ion $\eta^7\text{-}C_7H_7^+$ and thus classified as a 6-electron donor. However, recent studies have shown that the assignment of +1 formal charge to this ligand in its complexes is inappropriate. For example, it gives the misleading impression that the $\eta^7\text{-}C_7H_7$ ligand is more susceptible to nucleophilic attack than other coordinated polyenes; in fact, according to the Davies, Green, and Mingos rules,[54] it is the least susceptible to nucleophilic attack of all common coordinated polyenes. Moreover, X-ray photoelectron spectroscopy studies on $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ (M = Cr, V, or Ti) have showed that the oxidation state of the metal increases in the sequence Cr < V < Ti. In the Ti compound, there is greater localization of the negative charge on the C_7 ring (0.7–0.8 electrons) than on the C_5 ring (0.3–0.4 electrons).[55] Similar results have also been obtained from ab initio calculation,[56] metalation experiments,[57] and ^{13}C NMR studies on this type of compounds.[58]

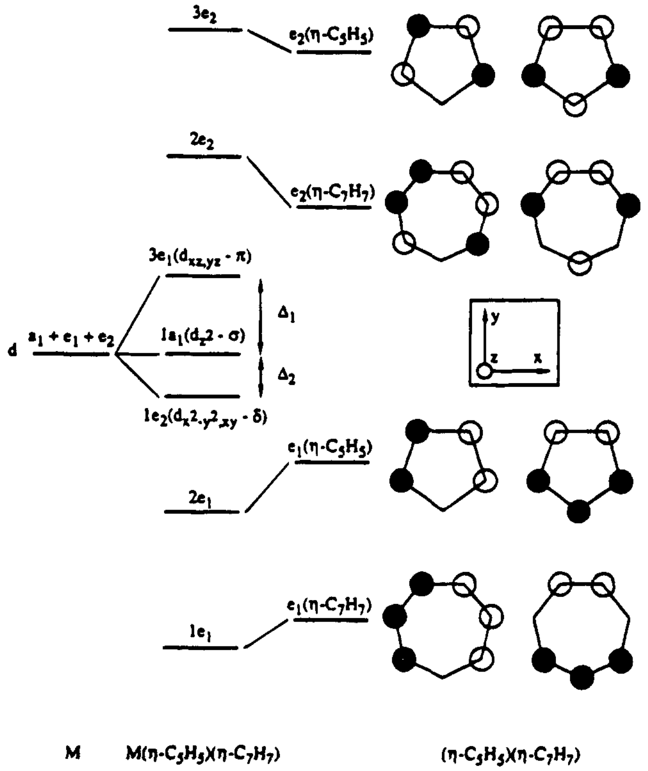
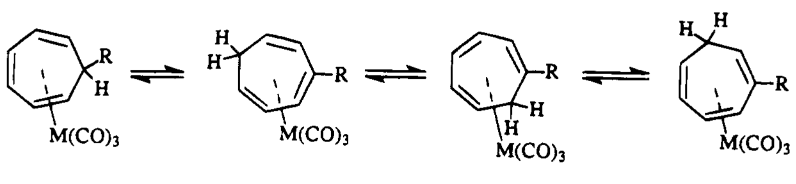


Figure 7. Qualitative molecular orbital diagram for $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$.

In an extensive study of $Ti(\eta^7\text{-}C_7H_7)$ chemistry,[22] Green *et al.* have found that the $Ti(\eta^7\text{-}C_7H_7)$ moiety is markedly reluctant to form any 18-electron complexes and it prefers to form 16-electron complexes $Ti(\eta^7\text{-}C_7H_7)L_2X$ where L is a 2-electron donor ligand and X is a 1-electron σ-bonded group. This observation is also not consistent with the common formulation of the cycloheptatrienyl group as $C_7H_7^+$. Since if the $\eta^7\text{-}C_7H_7$ group is given a formal charge of +1, the $[Ti(\eta^7\text{-}C_7H_7)]^+$ group might be expected, by analogy with $V(\eta^5\text{-}C_5H_5)$ which is also by definition d^4, to form 18-electron complexes such as $[Ti(\eta^7\text{-}C_7H_7)(CO)_4]^+$ [*cf.* $V(\eta^5\text{-}C_5H_5)(CO)_4$]. However, no complexes with π-acceptor ligands have been isolated.

In order to study the nature of the $M\text{-}(\eta^7\text{-}C_7H_7)$ bond, Green *et al.* have performed photoelectron (PE) spectroscopic studies on the sandwich compounds $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ (M = Ti, V, Nb, Cr, or Mo) and $Ta(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)$.[22b,37,59,60] Sandwich compounds have been chosen because they give rise to PE spectra with well-separated bands of metal, ligand, and mixed-metal/ligand character. A qualitative MO diagram for these sandwich compounds is shown in Figure 7 in which only the e symmetry pπ orbitals of the ligands are considered.[37] The metal d orbitals split into three sets; d_{z^2} ($1a_1$), d_{xz}, d_{yz} ($3e_1$) and $d_{x^2-y^2}$, d_{xy} ($1e_2$), which are of σ, π, and δ symmetry respectively with respect to the metal-ring axes. The

Scheme 17



$1a_1$ orbital is essentially non bonding. The $3e_1$ orbitals are strongly antibonding and the $1e_2$ orbitals are metal → carbon back-bonding in nature. Since the e_1 and e_2 orbitals of C_7 ring are lower than those of C_5 ring, the e_2 interaction will take place primarily via C_7 ring while the e_1 involvement remains predominantly with C_5 ring. Thus the localization of $1e_2$ MO's is of central importance in determining the nature of the $M-(\eta^7\text{-}C_7H_7)$ bond. If these orbitals are largely metal-localized, this implies that the metal → carbon back-bonding is relatively weak, whereas if there is a significant contribution from the ligand, the metal–ligand δ interaction is strong.

It has been shown by the PE data that for $Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$, the four least tightly bound electrons in $1e_2$ MO's are substantially localized on the C_7 ring, and have the primary role in forming the covalent bonds between the ring and the metal.[22b,59] Formally three of these electrons are derived from the metal and thus the compound is considered to have a Ti(IV) (d^0) metal center. Consequently, this description redefines the formal charge of the ligand $\eta^7\text{-}C_7H_7$ as -3. In which case the Hückel $4n + 2$ rule for aromaticity is still satisfied. The proposal is in accord with the general pattern of $Ti(\eta^7\text{-}C_7H_7)$ chemistry. The harder bases, such as ethers and amines, are more tightly bound to $[Ti(\eta^7\text{-}C_7H_7)]^+$ moiety than the softer bases, such as phosphines, indicating that the metal center is more d^0 than d^4 in character.

In contrast, by comparing the relative intensities of the photoelectron bands in the He I and He II spectra of group 5 sandwich compounds, it has been shown that the $1e_2$ level contains a significant contribution from both ligand and metal valence atomic orbitals.[37,59]

In a systematic PE spectroscopic study of $[M(\eta^m\text{-}C_mH_m)(\eta^n\text{-}C_nH_n)]$ (m, n = 5, 6, 7, or 8), it has been found that the ring contribution in the e_2 MO's increases with ring size and decreases with increase in the metal atomic number across the transition series.[59,61] The results are consistent with the observation that the negative charge on the C_7 ring in $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ (M = Cr, V, or Ti) follows the order: Ti > V > Cr.[55] Although the ligand contribution in the $1e_2$ MO's is smaller in $Cr(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ than in the Ti and V analogs, it has been noted that the a_1-e_2 splitting in $Cr(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ (1.6 eV) is substantially greater than that in $Cr(\eta^6\text{-}C_6H_6)_2$ (0.9 eV), suggesting the high contribution the C_7 ring e_2 orbitals makes to the e_2 MO's.[59]

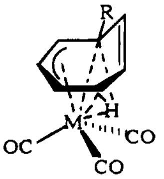
The relative metal and ligand contributions to the $1e_2$ MO's in these sandwich compounds has recently been estimated as around 60–80% metal character by using synchrotron radiation to provide access to a wide range of incident photon energies.[60] This indicates that neither the +1 nor −3 formalism for the charge on the cycloheptatrienyl ring is an accurate description of the metal–ring bonding in these complexes. Accordingly, it has been proposed that the η^7-cycloheptatrienyl ligand is best described as a 7-electron donor and a trivalent ligand and that three metal electrons are required to form the $M-(\eta^7\text{-}C_7H_7)$ covalent bond.

VI. Reactivity

A. Cycloheptatriene Metal Complexes

1. Sigmatropic Rearrangements

By using the deuterium-labeled cycloheptatriene-molybdenum complex $Mo(\eta^6\text{-}C_7H_7D\text{-}7)(CO)_3$, Roth and Grimme showed that the 7-*endo*-hydrogen migrates leading to an essentially complete deuterium scrambling. It was suggested that the process might involve initial migration of the hydrogen to the metal with formation of the cycloheptatrienyl molybdenum hydride species $Mo(\eta^7\text{-}C_7H_6D)(CO)_3H$.[62] The related processes for $Cr(\eta^6\text{-}C_7H_7R\text{-}7)(CO)_3$ (R = Me, Ph, or *p*-tolyl) was studied by Pauson *et al.* who confirmed that only the *exo*-isomers are capable of such rearrangement. However, the stepwise formation of the substituted derivatives and the stereospecificity of the rearrangement suggested that the overall process involves a series of sequential 1,5-hydrogen migrations (Scheme 17) and the transition state **29**.[63] This was further supported by the work by Brown *et al.* They prepared a tricarbonylmolybdenum complex with ^{13}C-labeled cycloheptatriene and then followed the thermolysis of this compound by ^{13}C NMR. The redistribution of isotopic label in the product was compared with that predicted from solving the differential equations describing the kinetics of each of the possible rearrangement pathways.[64] It was thus confirmed that a 1,5-hydrogen shift is involved. Low-temperature matrix isolation studies showed that thermal rearrangement of $Mo(\eta^6\text{-}C_7H_8)(CO)_3$ in the gas phase produces a new species which have $v(CO)$ at 1909, 1957, and 2042 cm^{-1}. It was proposed to be the metal hydride complex $Mo(\eta^5\text{-}C_7H_7)(CO)_3H$ (**30**).[65]



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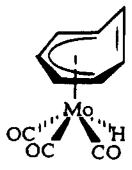
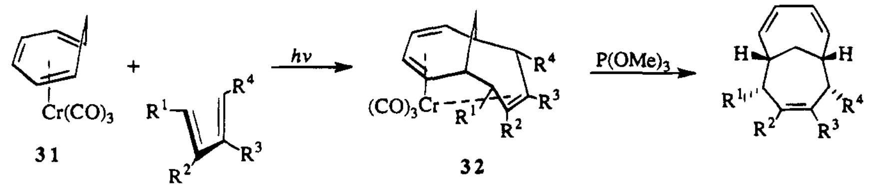


30

As mentioned in section III.A, the reaction of $Mo(CO)_6$ with 1,3,5,7-tetramethylcycloheptatriene gives a mixture of **1**, **2**, and **3** in 53, 21, and 8% yield, respectively (Scheme 2).[12] The formation of **2** and **3** may be ascribed to a series of sequential 1,5-hydrogen

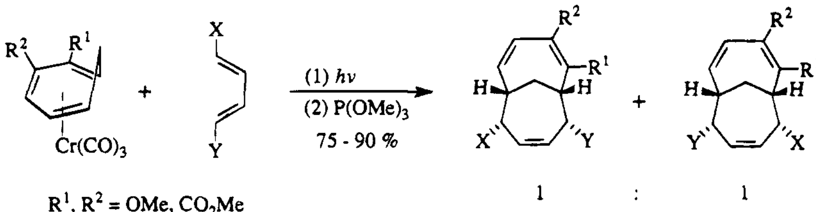
Scheme 18



31 **32**

R^1, R^4 = H, Me, CH=CH$_2$, CO$_2$Me
R^2, R^3 = H, Me

Scheme 19



R^1, R^2 = OMe, CO$_2$Me
X = H; Y = OSiMe$_3$
X = Me; Y = CO$_2$Me

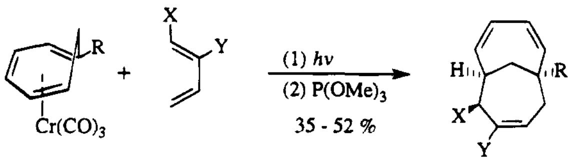
migrations in the initially formed **1**. This has been verified by heating a solution of pure **1** under similar conditions. The ^{1}H NMR spectrum of the resulting solution shows that it contains compounds **1**, **2**, and **3** in 6:2.5:1 ratio, which is close to that found in the initial reaction. It was suggested by Pauson *et al.* that substituents in the 1-position might hinder the formation of the proposed transition state **29**.[63b] Thus compounds having 1- and 6-substitution do not undergo further rearrangement as in the case of compounds **2** and **3**.

2. Cycloaddition Reactions

Higher order cycloaddition reactions ($6\pi + 4\pi$, $6\pi + 2\pi$, $4\pi + 4\pi$) usually proceed with a high level of stereoselectivity. However, the chemical yields of these reactions are relatively low due to the small periselectivity. For example, the thermal reactions of cycloheptatriene with dienes give a myriad of products of which the [6 + 4] adduct is only a minor component.[66] Kreiter *et al.* demonstrated that the cycloaddition reaction can be promoted by a transition metal.[67] The photochemical reactions of Cr(η^6-C$_7$H$_8$)(CO)$_3$ (**31**) with 1,3-butadiene and its derivatives give the bicyclo[4.4.1]undecane adducts **32** in good yields which can be demetalated by the action of P(OMe)$_3$ (Scheme 18).[68] These transition metal-mediated cycloadditions have been further elaborated by Rigby *et al.*[69] They have studied the regio- and stereoselectivity of these reactions by employing substituted derivatives of **31** and a range of substituted butadienes. Both electron-rich and electron-deficient dienes participate equally well in the transformation giving only the *endo* diastereomer. For 2- and 3-substituted cycloheptatriene complexes, the reactions show little regioselectivity which is exemplified in Scheme 19. However, for 1-substituted cycloheptatriene complexes, the reactions display high regioselectivity in some cases which are presumably due to steric factors (Scheme 20).[70]

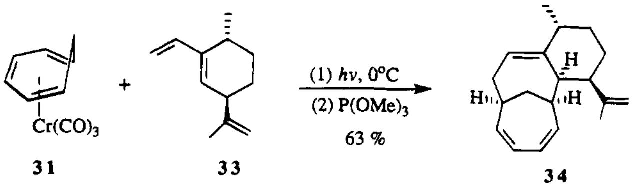
Diastereoselectivity has been observed for the photocycloaddition of **31** with optically pure dienes.[70,71]

Scheme 20



R = Me, OMe
X = Me, OSiMe$_3$; Y = H
X = H; Y = OSiBu^{t}Me$_2$

Scheme 21

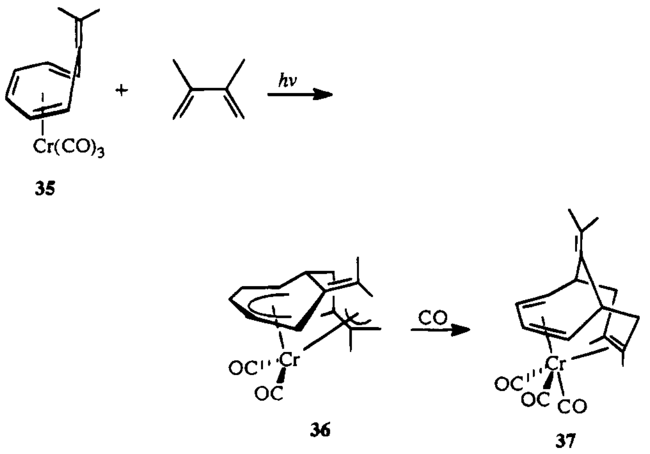


31 **33** **34**

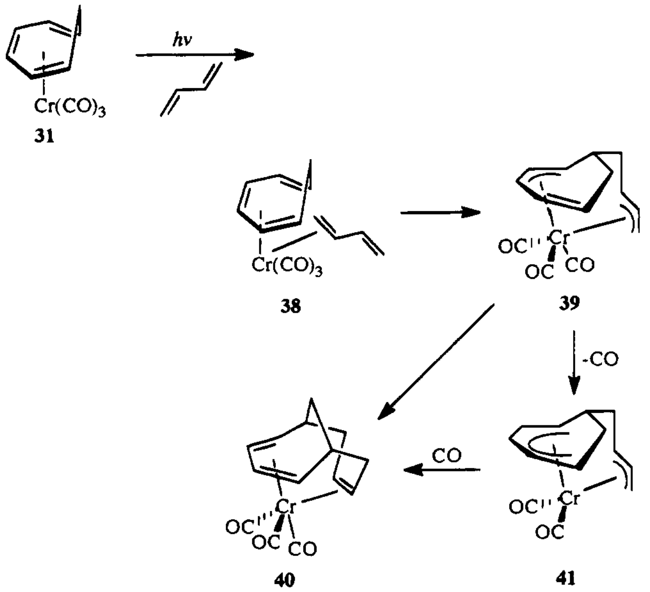
A promising example has been reported which involves the cycloaddition of **31** with diene **33**. The reaction gives **34** in 63% yield and less than 5% of its diastereomer could be detected (Scheme 21).[71]

It is worth noting that the photochemical reaction of heptafulvene complex **35** with 2,3-dimethyl-1,3-butadiene gives the unexpected product **36** in good yield. Treatment of **36** with CO (1 atm) at 0 °C results in the formation of the usual adduct **37** (Scheme 22).[72] This observation suggests that the chromium-mediated [6 + 4] cycloaddition is not a concerted reaction but a stepwise process. A plausible mechanism has been proposed which is illustrated in Scheme 23.[67,72b] The first step is a light-induced η^6 to η^4 hapticity change of the triene ligand, leaving a vacant site to which the diene is coordinated. Then a C–C coupling occurs between the diene and the C(1) atom in the cycloheptatriene giving the complex **39**. A further C–C coupling gives the cycloadduct **40**, while loss of a CO produces the η^3,η^5-complex **41**. The mechanism has been reexamined by Stufkens *et al.*, who study the primary photoprocesses in low-temperature matrices and the

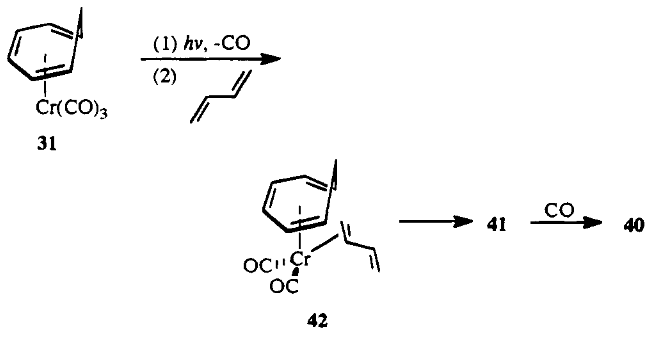
Scheme 22



Scheme 23

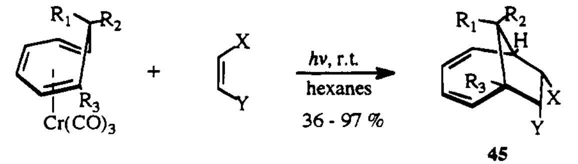


Scheme 24



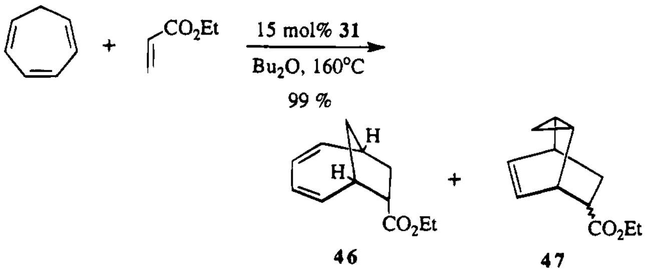
secondary thermal reactions in liquefied noble gases with infrared spectroscopy.[73] Although both CO loss and η^6 to η^4 hapticity change of the triene ligand have been observed, in solution, only the CO loss gives rise to the coupling reaction. Accordingly, an alternative mechanism has been proposed (Scheme 24). Light-induced ejection of CO produces the coordinatively unsaturated complex $Cr(\eta^6\text{-}C_7H_8)(CO)_2$, which binds to the diene forming **42**. A C−C coupling followed by recapture of the dissociated CO leads to the adduct **40**.

Scheme 25



R^1, R^2, R^3 = H, Me, Bu, OMe
X = H, CO_2Et
Y = COMe, CO_2Et, SOPh, SO_2Ph, CN

Scheme 26

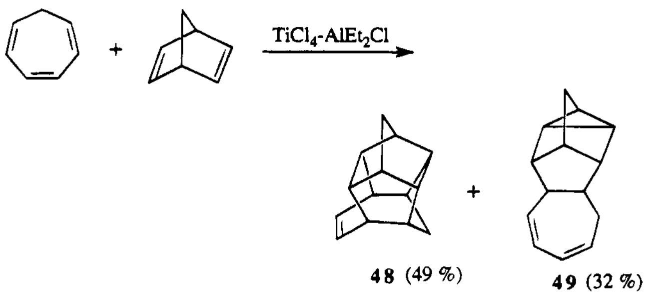


The molybdenum and tungsten congeners $M(\eta^6\text{-}C_7H_8)(CO)_3$ [M = Mo (**43**) or W (**44**)] have also been examined as substrates in the photoinduced [6 + 4] cycloaddition reaction.[70] The molybdenum complex **43** also promotes the cycloadditions but the chemical yields are uniformly lower than those for the chromium reactions. This has been rationalized by the weaker bond strength of $Mo-C_7H_8$ bond. Presumably, the complex strips of the metal center readily and thus does not effectively participate in the cycloaddition process. The tungsten analog **44** is totally ineffective for promoting the cycloadditions which may due to the fact that **44** has the strongest metal−ligand bonding in the group 6 series.[74]

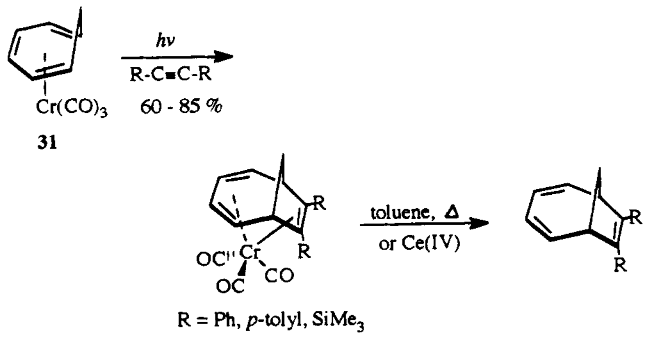
The related photoinduced [6 + 2] cycloaddition has also been reported.[75,76] Irradiation of a mixture of **31** or its derivatives and electron-deficient alkenes in hexanes at room temperature gives the metal-free bicyclo[4.2.1]nonadiene adducts **45** in good yields (Scheme 25). The reactions afford a single diastereomer resulting from an *endo* approach of the trienophile. It is noted that reactions with electron-rich alkenes do not give the desired adducts. This may be related to the strength of metal−alkene bond in the intermediate analogous to **42** that is presumably involved in these transformations. The electron-donating groups on the 2π partner diminish the d-π^* back-bonding, thus weaken the metal−alkene bond.

These [6 + 4] and [6 + 2] cycloadditions can also be effected by thermal activation. Heating complex **31** with dienes or alkenes in refluxing di-*n*-butyl ether affords high yields of the corresponding metal-free adducts directly.[70,76,77] The products obtained by this means are identical in every respect to those obtained in the photochemical reactions. Interestingly, the same transformations can also be achieved by using a catalytic amount of a transition metal complex. For example, heating cycloheptatriene with excess ethyl acrylate in the presence of 15 mol % of **31** gives a mixture of **46** and **47** in 10:1 ratio and 99% yield (Scheme 26). Using smaller amounts of **31** (2 mol %) results in enhanced discrimination in the formation of **46** and **47** (98:2) but in a lower yield (55%).[76,77] The reaction of cycloheptatriene with an excess of 1-acetoxy-1,3-butadiene in the presence of

Scheme 27



Scheme 28



ca. 30 mol % Cr(η^6-C_7H_8)(PPh_3)$(CO)_2$ generates the expected adduct in 36% yield.[70] The cycloaddition of cycloheptatriene with 1,3-butadiene and norbornadiene can also be catalyzed by the $TiCl_4$−$AlEt_2Cl$ system.[78a] The former reaction gives the [6 + 2] and [6 + 4] adducts in 78 and 8% yield, respectively, while the latter reaction affords compound **48** and the [2 + 2 + 2] adduct **49** (Scheme 27). The formation of **48** is attributed to a [6 + 2] cycloaddition followed by an intramolecular Diels-Alder reaction.

The [6 + 2] cycloadditions can be extended to alkynes as trienophiles. Photolysis of **31** and alkynes results in the formation of the corresponding adducts which can be decomplexed with either toluene at elevated temperature or Ce(IV) ion (Scheme 28).[79,80] The [6 + 2] cycloaddition of cycloheptatriene to phenyl(trimethylsilyl)acetylene can also be catalyzed by the catalytic system $TiCl_4$−$AlEt_2Cl$.[78b]

3. Lewis Base Addition Reactions

The 16-electron complex Zr(η^6-C_7H_8)$_2$ (**16**) is stable to hydrogen migration in the absence of Lewis base which is in contrast to the related titanium and molybdenum compounds. However, treatment of compound **16** with CO, Sn_2Me_6, or tmeda produces compound Zr(η^7-C_7H_7)(η^5-C_7H_9) (**50**) in excellent yields. The reaction between **16** and PMe_3 behaves differently. It gives compound **51**, a thermally sensitive PMe_3 adduct of **50**. The related reaction of **16** with dmpe leads to the thermally unstable Zr(η^4-C_7H_8)$_2$(dmpe) (**52**), which is rapidly converted into the dimer **53** at room temperature. The compound **53** can also be directly prepared by treating compound **50** with dmpe (Scheme 29).[24]

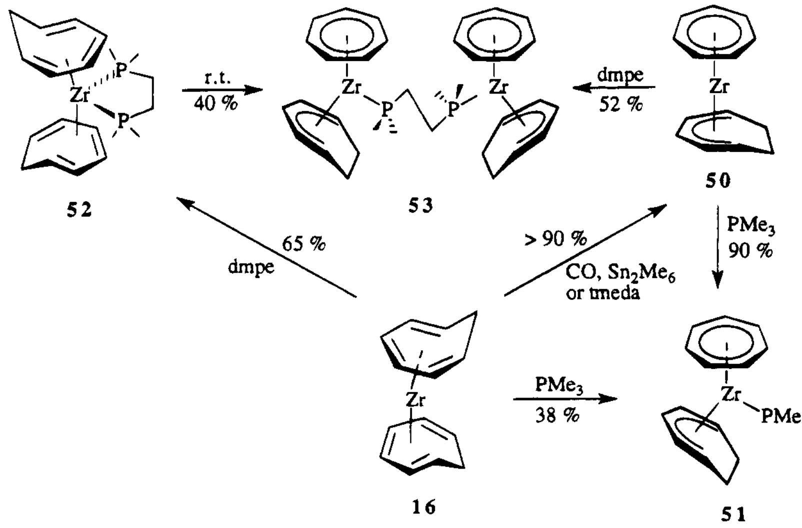
4. Ligand Exchange Reactions

The cycloheptatriene ring in M(η^6-C_7H_8)$(CO)_3$ [M = Cr (**31**), Mo (**43**), or W (**44**)] is relatively labile and can be displaced with a wide range of neutral ligands. The enthalpies of substitution of the complexes M(η^6-C_6H_6)$(CO)_3$ (M = Cr, Mo, or W) with cycloheptatriene have recently been determined by solution calorimetry.[81] The values ($-\Delta H$, kJ/mol) increase from Cr (27.2) to Mo (38.0) to W (53.1) showing that the M−C_7H_8 bond strength increases down the group. The ease of release of the cycloheptatriene ring in substitution reactions, however, was observed to decrease down the series Mo > W > Cr.[82]

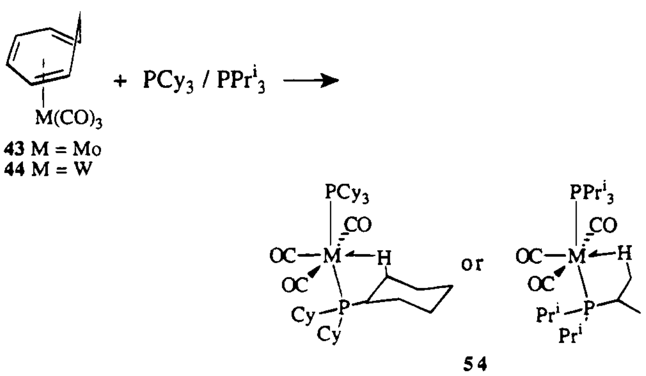
The reaction of **43** or **44** with the bulky phosphines PCy_3 or PPr^i_3 results in the formation of the formally five-coordinate, 16-electron complexes M$(PR_3)_2(CO)_3$ (**54**) (M = Mo or W; R = Cy or Pr^i) (Scheme 30).[83] The structures of the tungsten complexes have been determined which show the presence of agostic C−H⇀M interactions. It is worth mentioning that these molecules add dihydrogen to form stable η^2-H_2 complexes.[84] Thus, they represent rare examples in which both C−H and H−H bond activation occur at a single metal center.

Treatment of **31** with PR_3 (R = Cy or Pr^i) does not lead to the chromium analog Cr$(PR_3)_2(CO)_3$ (**55**). However, by employing Cr(η^6-naphthalene)$(CO)_3$ as the starting material, the reaction gives **55** (R = Cy)

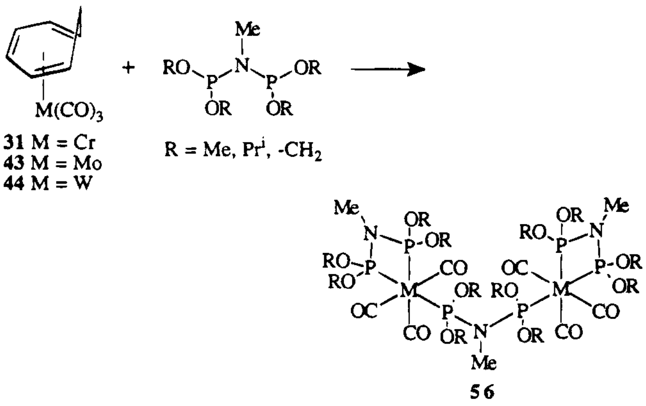
Scheme 29



Scheme 30



Scheme 31



in good yield.[85] Failure to produce **55** from **31** may be due to thermodynamic factors. Since the reactions of Cr(η^6-naphthalene)(CO)$_3$ with various ligands are about 40 kJ/mol more exothermic than analogous reactions of **31**, this may provide the additional driving force necessary for forming **55**.

Compound Mo(η^6-C$_7$H$_8$)(CO)$_3$ (**43**) reacts with tris(2,4,6−trimethoxyphenyl)phosphine (TMPP) to give Mo(η^3-TMPP)(CO)$_3$ of which the molecular structure shows an octahedral geometry with the TMPP ligand bound to the metal in tridentate mode with the phosphorus atom and two of the methoxy groups.[86a]

Reaction of **31** with bidentate ligands Ph$_2$PCH$_2$CH$_2$AsPh$_2$ (ape) and Ph$_2$AsCH$_2$CH$_2$AsPh$_2$ (dae) affords *mer*-Cr(CO)$_3$(η^1-ape)(η^2-ape) and *fac*-Cr(CO)$_3$(η^1-dae)(η^2-dae), respectively. The monodentate ape ligand in the former complex is coordinated through phosphorus as shown by ^{31}P NMR studies.[86b]

Displacement of C$_7$H$_8$ ligand in **31**, **43**, and **44** with other novel ligands has also been reported. For example, the reaction of these compounds with the ligands MeN[P(OR)$_2$]$_2$ (R = Me, Pr^i, or −CH$_2$) leads to the ligand-bridged dimers **56** in *all-mer, all-fac*, and *mer-fac* forms depending on the ligand and conditions used (Scheme 31).[87] For M = W, the reactions also yield the novel cycloheptatriene-bridged dimers *mer*-{W(CO)$_3${MeN[P(OR)$_2$]$_2$}}$_2$(μ-η^2:η^2-C$_7$H$_8$) (**57**) as minor products. The structure of **57** (R = Me) (Figure 8) confirms that the two metal fragments bond to the two nonadjacent carbon−carbon double bonds in the cycloheptatriene ring, which adopts a tub conformation with the metal moieties on the same face.[88]

The reaction of **43** with the diphosphabenzene **58** leads to C$_7$H$_8$ substitution giving the complex **59**, which has been structurally characterized (Scheme 32).[89a] The heterocycle **58** is coordinated to the metal via the methallylic π-system and via the semiylidic carbon atom. The product **59** thus preserves a 18-electron configuration. Displacement of C$_7$H$_8$ ring from **43** by K$_3$E$_7$ (E = P, As, or Sb) has recently been reported.[89b] The reactions give the trianions [Mo(CO)$_3$E$_7$]$^{3-}$, which comprise distorted norbornadiene-like η^4-E$_7$$^{3-}$ groups bound to Mo(CO)$_3$ center.

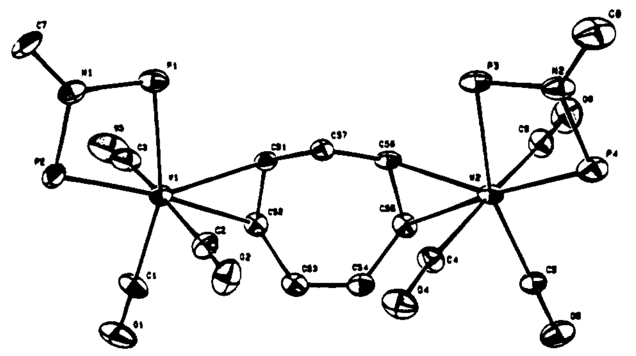
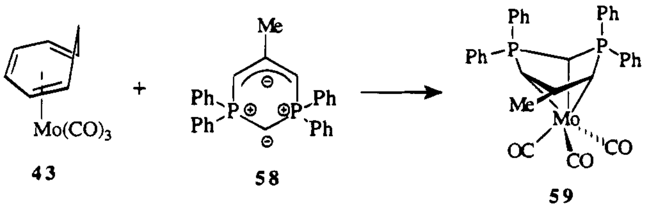
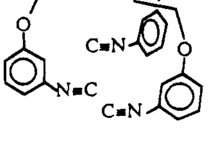


Figure 8. Molecular structure of *mer*-{W(CO)$_3${MeN-[P(OMe)$_2$]$_2$}}$_2$(μ-η^2:η^2-C$_7$H$_8$). Methoxy group omitted for clarity.

Scheme 32



The tripodal triisocyanide ligands **60**-**62** can also displace the cycloheptatriene ring in **31**, **43**, and **44** to give the corresponding chelate complexes *fac*-M(CO)$_3$L.[90] Treatment of **43** with molar equivalence of PPh$_3$, Et$_3$N, and picolinic or quinaldinic acid also leads to ring displacement producing the salt [Et$_3$NH][Mo(CO)$_3$(PPh$_3$)L] (L = 2-picolinate or 2-quinaldinate).[91]



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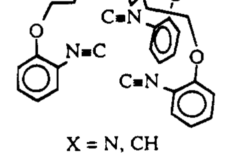

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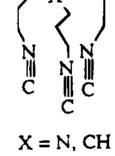
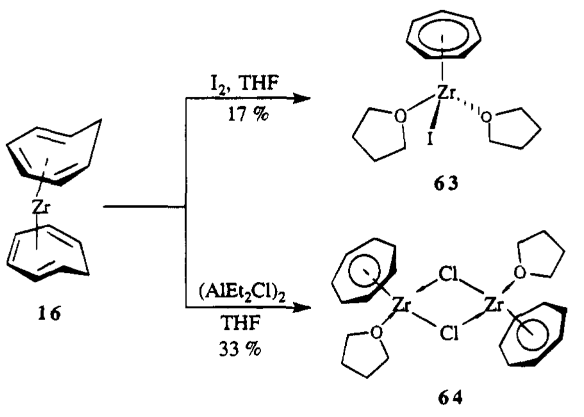


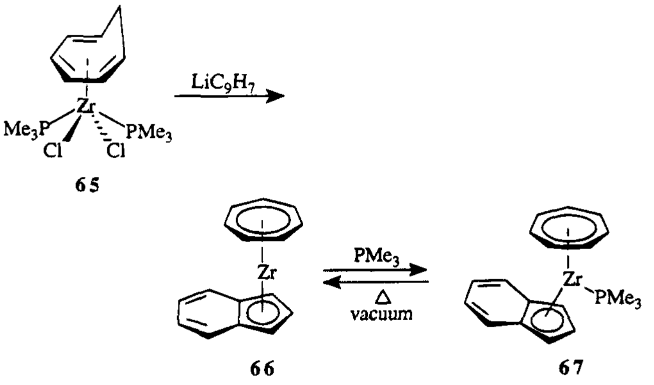
62

Thermal substitution of the CO ligand in **31**, **43**, and **44** is rare and only one example was reported.[92] In contrast, photoinduced CO substitutions for these complexes are well-documented. Irradiation of the chromium complex **31** in the presence of neutral ligands L, such as PPh$_3$, PMe$_3$, AsMe$_3$, P(OMe)$_3$, or P(OPh)$_3$ gives the complexes Cr(η^6-C$_7$H$_8$)(CO)$_2$L.[93] The photochemistry of **31** and the molybdenum analog **43** in low-temperature gas matrices has been studied by Rest *et al.*[94,95] Infrared spectroscopic studies show that UV irradiation of these compounds in CH$_4$ and Ar matrices at 12 K leads to ejection of CO to form the coordinatively unsaturated M(η^6-C$_7$H$_8$)(CO)$_2$ in a reversible manner. Photolysis of **31**

Scheme 33



Scheme 34



or **43** in a N_2 matrix produces the dinitrogen complexes $M(\eta^6\text{-}C_7H_8)(CO)_2N_2$. In a CO matrix, stepwise photoelimination of cycloheptatriene occurs to give $M(CO)_6$ via the intermediate species $M(\eta^4\text{-}C_7H_8)(CO)_4$.

5. Redox Reactions

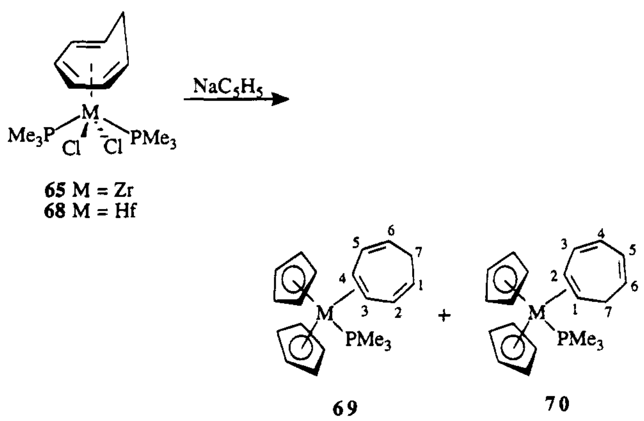
The electrochemistry of **31**, **43**, and **44** has been examined at a Pt electrode in aprotic solvents.[96] The study shows that this series of compounds have a different electrochemical behavior depending on the solvent. All of them are converted into $M(CO)_6$ via the cations $[M(\eta^6\text{-}C_7H_8)(CO)_3]^+$ after electrolysis at the appropriate potential in acetonitrile. In dichloromethane, the monocations can also be detected. But their conversion into $M(CO)_6$ has not been observed.

Cyclic voltammetric study of $Mo(\eta^6\text{-}C_7H_8)_2$ (**6**) shows that it undergoes a reversible 1-electron oxidation at $E_{1/2} = -0.43$ V *vs* ferrocenium–ferrocene couple. Chemical oxidation of **6** can be achieved by the action of $AgBF_4$, giving the cation $[Mo(\eta^6\text{-}C_7H_8)_2]^+$ (**8**). Reduction of **8** with sodium amalgam regenerates the neutral compound **6**.[21]

Oxidation of $Zr(\eta^6\text{-}C_7H_8)_2$ (**16**) with iodine in THF leads to the formation of $Zr(\eta^7\text{-}C_7H_7)(THF)_2I$ (**63**),[26b,27] whereas reaction of **16** with $(AlEt_2Cl)_2$ in THF produces the dimer **64** (Scheme 33).[24]

Treatment of $Zr(\eta^6\text{-}C_7H_8)(PMe_3)_2Cl_2$ (**65**) with an excess of lithium indenide affords a mixture of the sandwich compound $Zr(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_9H_7)$ (**66**) and its PMe_3 adduct **67** (Scheme 34). Recrystallization of the mixture in the presence of PMe_3 results in the isolation of pure **67**. This compound is thermally unstable and on heating under vacuum, it evolves PMe_3 to give **66**. The reaction with the hafnium analog $Hf(\eta^6\text{-}C_7H_8)(PMe_3)_2Cl_2$ (**68**) gives similar results, except that the hafnium phosphine adduct $Hf(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_9H_7)(PMe_3)$ is thermally more robust than its zirconium counterpart **67**.[28]

Scheme 35



Compounds **65** and **68** also react with sodium cyclopentadienide giving an inseparable mixture of isomers **69** and **70** (Scheme 35). The crystal structure of the major isomer **69** (M = Zr) reveals that the C_7H_8 ligand is η^2-bonded to the metal by the C(3) and C(4) carbons. At elevated temperature, the reaction of **65** with sodium cyclopentadienide gives the dimer $[Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}\sigma{:}\eta^5\text{-}C_5H_4)(PMe_3)]_2$ in 14% yield.[28]

In contrast, the reaction of $Nb(\eta^6\text{-}C_7H_8)(PMe_3)_2Cl_2$ (**20**) with an excess of NaC_5H_4R (R = H or Me) yields the paramagnetic sandwich compounds $Nb(\eta^7\text{-}C_7H_7)$-

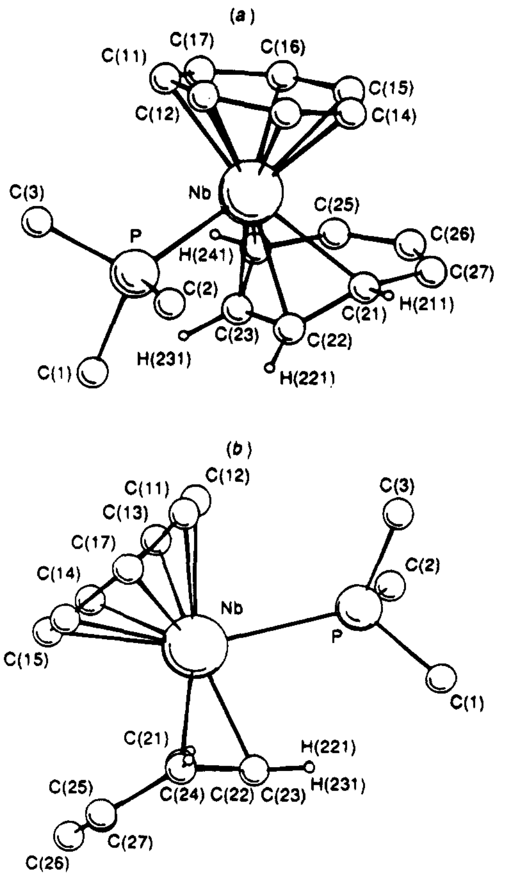
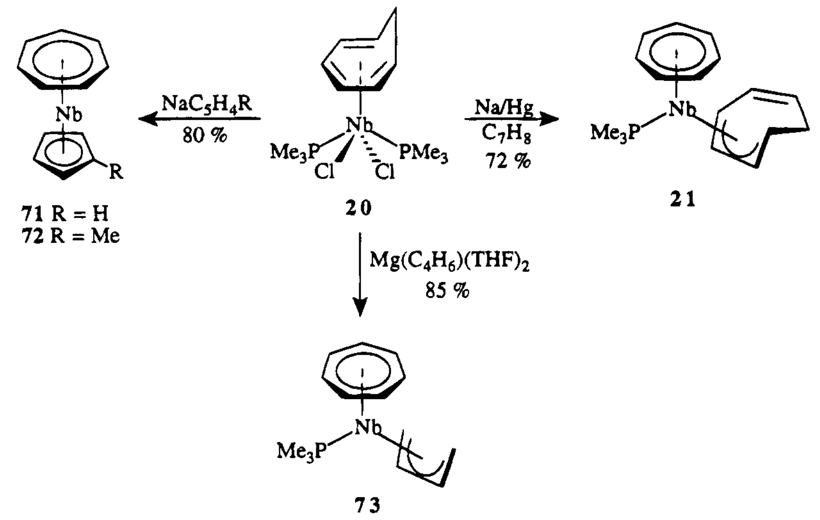
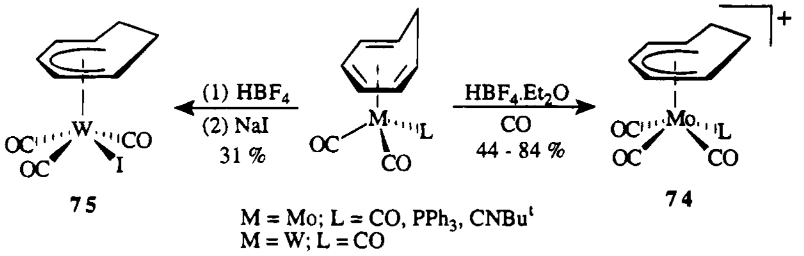


Figure 9. Molecular structure of $Nb(\eta^7\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)$. Most hydrogen atoms omitted.

Scheme 36



Scheme 37



(η^5-C$_5$H$_4$R) [R = H (**71**) or Me (**72**)] as the sole product. Reduction of **20** with excess sodium amalgam and cycloheptatriene leads to the η^4-cycloheptatriene complex **21** in good yield. Figure 9 shows the molecular structure of **21**, in which the coordinated C$_4$ fragment is essentially planar and the contribution of a metallacyclopentene structure in **21** is relatively small. Treatment of **20** with the magnesium butadiene complex Mg(C$_4$H$_6$)(THF)$_2$ causes reductive substitution of metal chlorides giving Nb(η^7-C$_7$H$_7$)(η^4-C$_4$H$_6$)(PMe$_3$) (**73**) (Scheme 36).[35]

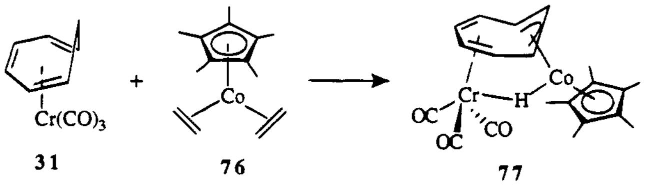
6. Other Reactions

Protonation of M(η^6-C$_7$H$_8$)(CO)$_3$ [M = Mo (**43**) or W (**44**)] with HBF$_4$ produces the 16-electron cations [M(η^5-C$_7$H$_9$)(CO)$_3$]$^+$ while protonation with HCl leads to the formation of the neutral complexes M(η^5-C$_7$H$_9$)(CO)$_3$Cl.[97] In the presence of a vigorous stream of carbon monoxide, the reaction of Mo(η^6-C$_7$H$_8$)(CO)$_2$L (L = CO, PPh$_3$, or CNBu^t) with HBF$_4$·Et$_2$O gives the cycloheptadienyl cations [Mo(η^5-C$_7$H$_9$)(CO)$_3$L]$^+$ (**74**) (Scheme 37).[98a,b] The tungsten analog of **74** cannot be obtained by this method. However, treatment of **44** with HBF$_4$ followed by reaction with NaI affords moderate yield of W(η^5-C$_7$H$_9$)(CO)$_3$I (**75**) (Scheme 37).[98a]

Addition of potassium triethyl borohydride to M(η^6-C$_7$H$_8$)(CO)$_3$ [M = Cr (**31**) or Mo (**43**)] yields the salts [K][M(η^5-C$_7$H$_9$)(CO)$_3$], which react with R$_3$SnCl (R = Me or Ph) and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide to give M(η^5-C$_7$H$_9$)(CO)$_3$SnR$_3$ and M(η^5-C$_7$H$_9$)(CO)$_2$(NO), respectively.[98c]

The reaction of **31** with Co(η^5-C$_5$Me$_5$)(η^2-C$_2$H$_4$)$_2$ (**76**) affords the unusual heterobimetallic complex **77** in 15–25% yield (Scheme 38).[99] The reaction involves a change in hapticity of the seven-membered ring, loss of ethene, and a hydrogen shift. Upon treatment with CO, compound **77** regenerates **31** and gives Co(η^5-C$_5$Me$_5$)(CO)$_2$. The structure of **77** (Figure 10) shows that the bridging cycloheptatriene bonds to the Cr and Co in a η^4- and η^3-manner, respectively, and adopts a boat conformation. A bridging hydrogen is also present which allows both metals to attain an 18-electron configuration. Low-temperature ^{1}H and

Scheme 38



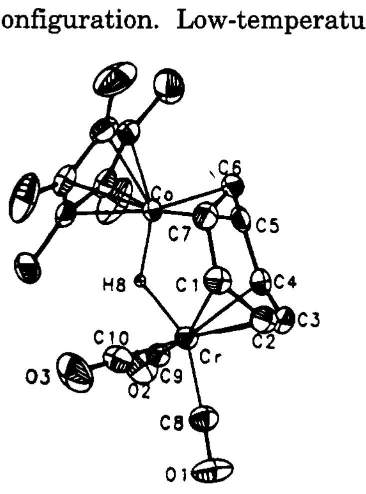
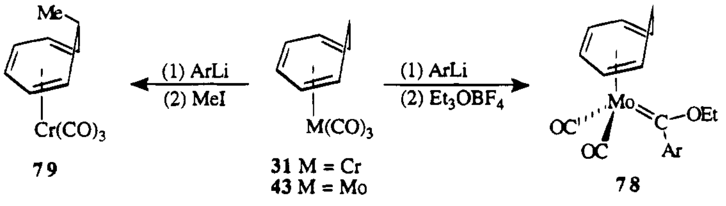


Figure 10. Molecular structure of Cr(CO)$_3$(μ-η^4:η^3-C$_7$H$_7$)(μ-H)Co(η^5-C$_5$Me$_5$).

Scheme 39



Ar = C_6H_5, p-$CF_3C_6H_4$, o- or p-$CH_3C_6H_4$

^{13}C NMR spectra of **77** exhibit signal patterns corresponding to a rigid μ-η^4:η^3-C_7H_7 structure. This is in contrast to those of the related *syn*-M(μ-C_7H_7)M′ complexes in which the rotation of the C_7H_7 ring cannot be frozen out.[100]

Treatment of **43** with aryllithium at low temperature followed by the addition of Et_3OBF_4 gives the cycloheptatriene carbene complexes **78** (Scheme 39). For the chromium analog **31**, the reaction proceeds only with p-$CF_3C_6H_4Li$. Other aryllithium compounds, such as C_6H_5Li, o- or p-$CH_3C_6H_4Li$, cause deprotonation at the C(7) carbon atom of the cycloheptatriene ring giving *exo*-Cr(η^6-C_7H_7Li-7)$(CO)_3$. Alkylation with iodomethane gives the substituted cycloheptatriene complex **79** (Scheme 39).[101a]

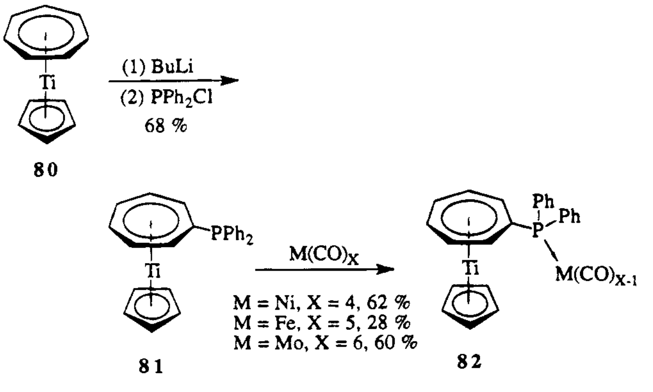
The gas-phase ion chemistry of **31** has recently been studied by Fourier transform ion cyclotron resonance spectroscopy.[101b] The ion reactivities parallel the electron deficiencies of the central metal atoms and show the order $Cr^+ > C_5H_6Cr^+ > C_7H_8Cr^+ \approx C_7H_8Cr(CO)^+ > C_7H_8Cr(CO)_2^+ > C_7H_8Cr(CO)_3^+$. The ion $C_7H_8Cr^+$ has an anomalously low reactivity which has been explained by a β-hydride shift from the cycloheptatriene ring to the chromium atom that decreases the electron deficiency on the central metal.

B. Cycloheptatrienyl Metal Complexes

1. Lithiation Reactions

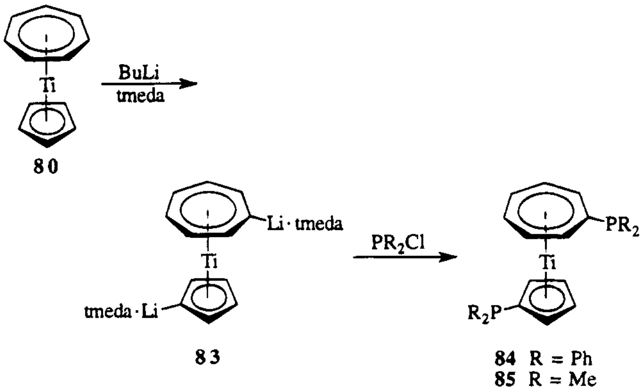
It was reported that lithiation of the sandwich compound Ti(η^7-C_7H_7)(η^5-C_5H_5) (**80**) occurs preferentially at the seven-membered ring. Addition of electrophile to the resulting lithiated species leads to selective functionalization of the cycloheptatrienyl ligand.[57] Thus treatment of **80** with 1 equiv of n-butyllithium in ether followed by the addition of 1 equiv of PPh_2Cl affords the phosphine containing titanium compound **81** (Scheme 40). The phosphorus group in **81** retains its nucleophilic and coordinating properties and its donating capability is slightly stronger than that of PPh_3. It displaces one carbonyl of $Ni(CO)_4$, $Fe(CO)_5$, and $Mo(CO)_6$ forming the bimetallic complexes **82** (Scheme 40).[102]

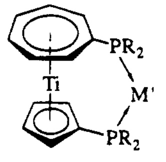
Scheme 40



Dimetalation of **80** can be achieved with 2.5 equiv of butyllithium–tmeda in hexane giving the highly air-sensitive dilithium derivative **83**. A subsequent reaction between **83** and 2 equiv of PR_2Cl (R = Ph[103] or Me[104]) produces diphosphines **84** or **85** (Scheme 41). These compounds react with various metal carbonyls of Cr, Mo, Mn,[105] Fe, and Co to produce a series of chelated heterobimetallic compounds Ti(η^7-$C_7H_6PR_2$)(η^5-$C_5H_4PR_2$)M′ (**86**) [for R = Ph, M′ = $Cr(CO)_4$, $Mo(CO)_4$, $Mn(CO)_3H$, $Fe(CO)_3$ or Co(η^5-C_5H_5); for R = Me, M′ = $Cr(CO)_4$ or $Mo(CO)_4$]. However, reaction between **85** and $Fe_2(CO)_9$ under similar

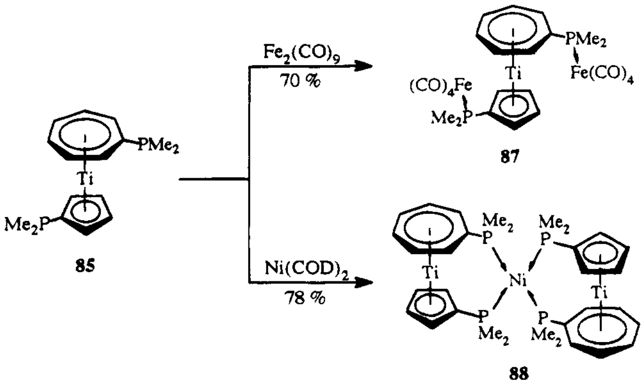
Scheme 41



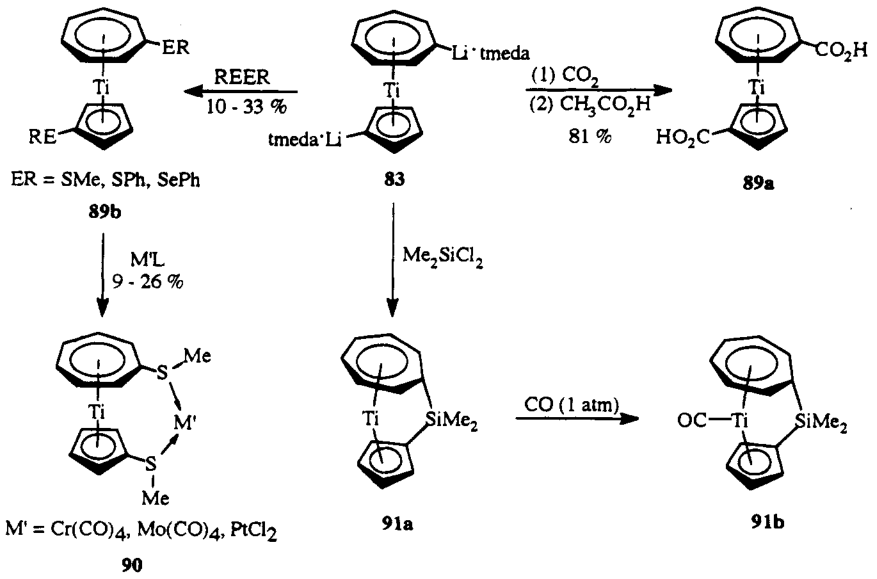


86

Scheme 42



Scheme 43



conditions gives the nonchelated product **87**. The phosphine ligands in **85** can also displace the COD ligands in $Ni(COD)_2$ giving the Ni(0) complex **88** (Scheme 42). The molecular structures of $Ti(\eta^7\text{-}C_7H_6\text{-}PR_2)(\eta^5\text{-}C_5H_4PR_2)Cr(CO)_4$ (R = Ph or Me) and $Ti(\eta^7\text{-}C_7H_6PPh_2)(\eta^5\text{-}C_5H_4PPh_2)Mn(CO)_3H$ have been elucidated, which show the insensitivity of the titanium sandwich structure to coordination of the phosphine ligands.[103–105]

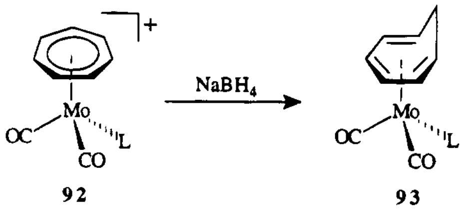
The mono- and dilithiated derivatives of **80** also react with other electrophiles.[106,107] For example, treatment of **83** with CO_2 followed by acidification gives the diacid **89a**,[106a] whereas the reaction of **83** with RSSR (R = Me or Ph) or PhSeSePh produces the sulfur or selenium derivatives **89b**.[106b] Compound **89b** (ER = SMe) reacts with $M(\eta^4\text{-norbornadiene})(CO)_4$ (M = Cr or Mo) or $Pt(C_6H_5CN)_2Cl_2$, giving the chelated complexes **90**. Treatment of **83** with Me_2SiCl_2 leads to the dimethylsilyl-bridged complex **91a**, which reacts with CO at ambient pressure to form the monocarbonyl complex **91b** (Scheme 43). It is worth noting that **80** does not carbonylate even at 14000 kPa.[107]

2. Nucleophilic Attack on η-C_7H_7 Ring

The C_7 ring in cationic cycloheptatrienyl complexes is susceptible to nucleophilic attack. For example, treatment of $[Mo(\eta^7\text{-}C_7H_7)(CO)_2L]^+$ [L = $P(OMe)_3$ or $CNBu^t$] (**92**) with $NaBH_4$ results in the formation of $Mo(\eta^6\text{-}C_7H_8)(CO)_2L$ (**93**) (Scheme 44).[98b,108] Substitution of CO in $[Mo(\eta^7\text{-}C_7H_7)(CO)_3]^+$ with a σ-donor L followed by nucleophilic attack is a commonly used method to prepare the otherwise inaccessible L-substituted compounds $Mo(\eta^6\text{-}C_7H_7R\text{-}7)(CO)_2L$ (R = H or alkyl).[109]

Substituted anilines, $XC_6H_4NH_2$ (X = H, 2-Me, 4-Me, or 2-Cl), add to the C_7 ring of $[W(\eta^7\text{-}C_7H_7)(CO)_3]^+$ (**94**) giving the corresponding cycloheptatriene adducts $W(\eta^6\text{-}C_7H_7\text{-}NHC_6H_4X\text{-}7)(CO)_3$ (**95**). Kinetic studies show that the reactions occur via a rapid preequilibrium formation of a π-complex followed by a rate-determining rearrangement to the cationic triene intermediate **96**, which rapidly loses a proton with the aid of amine or solvent to form the product **95** (Scheme 45). For the reaction with cyclohexylamine, the cationic intermediate is formed directly in a rapid preequilibrium, followed by competing rate-determining amine- and solvent-assisted proton removal.[110]

Scheme 44

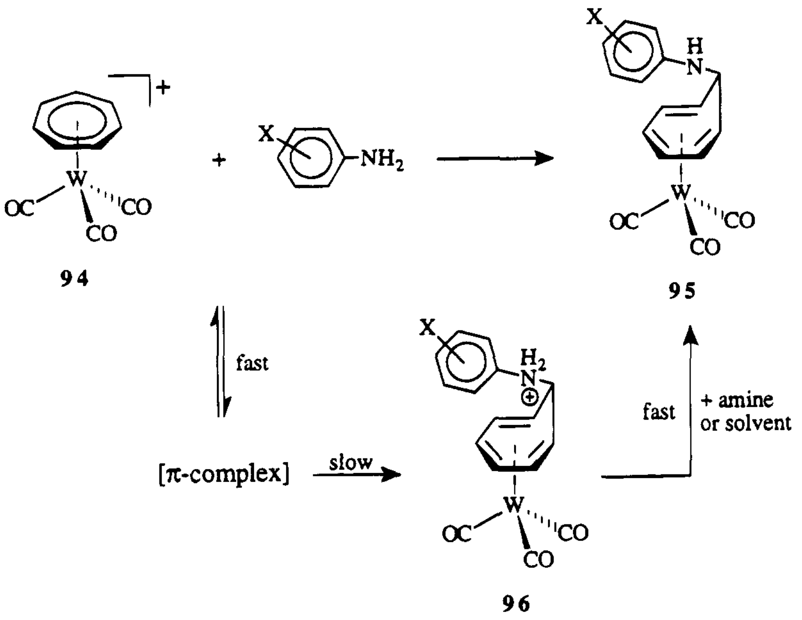


L = $P(OMe)_3$ (46 %), $CNBu^t$(54 %)

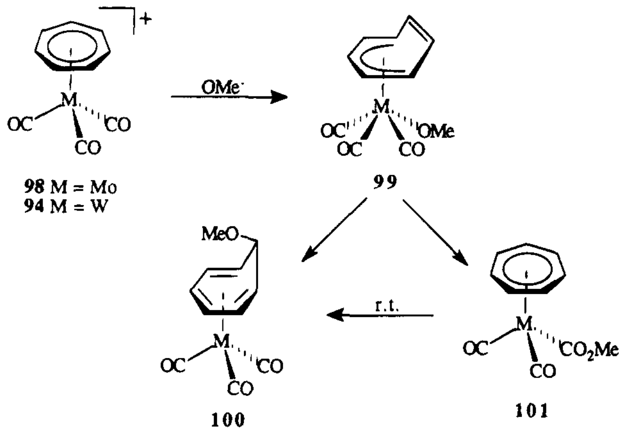
The reaction of $[M(\eta^7\text{-}C_7H_7)(CO)_3]^+$ [M = Cr (**97**), Mo (**98**), or W (**94**)] with methoxide ion has been studied in detail. Low-temperature IR and NMR spectroscopy have revealed that the reactions for Mo and W involve an initial attack at the metal forming **99** followed by dissociation to give both the thermodynamically stable 7-*exo* adducts **100** and the carbomethoxy species **101**. The latter compounds are quite stable at low temperature, but rearrange to **100** at room temperature (Scheme 46). The related chromium analogs of **99** and **101** could not be detected.[111] Theoretical calculations have also predicted the initial metal attack for these reactions.[112] Further evidences have been provided by the kinetic studies with stopped-flow spectrophotometry. Two separate processes have been identified. The first one involves a fast reversible formation of either **99** or **101**, while the second slower process involves methoxy ion attack to the C_7 ring for which the second rate constants are in the ratio 50:10:1 (Cr:Mo:W).[113]

The relative rates of methoxide ion transfer from methoxymalachite green $(p\text{-}Me_2NC_6H_4)_2CPhOMe$ to **97, 98,** and **94** are 1:10:6 (Cr:Mo:W), which are much slower than that of the reaction between $C_7H_7^+$ and methoxide (k_2^{rel} = 110).[114] π-Complexation of the $C_7H_7^+$ cation with a $Cr(CO)_3$ also greatly reduces its

Scheme 45



Scheme 46

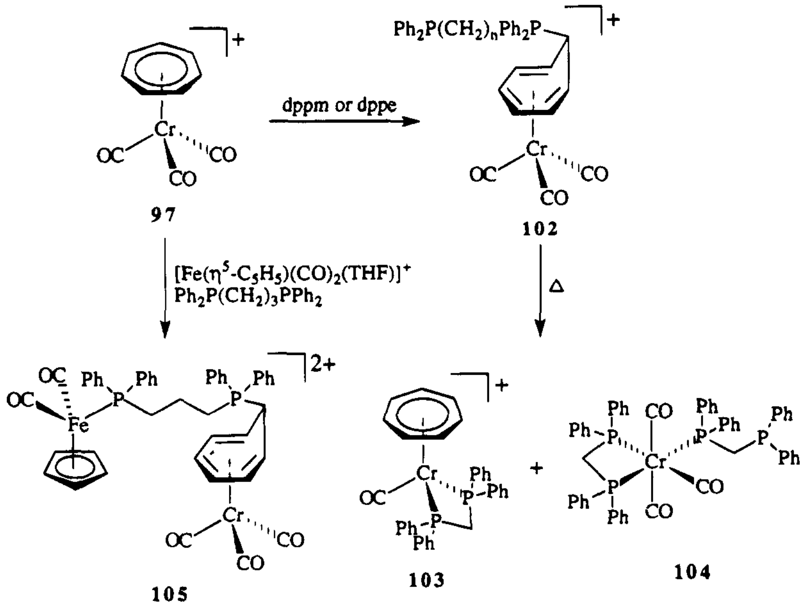


reactivity toward addition of methanol. The rate constant for this reaction as well as its reverse process, protonation of the 7-*exo* methoxy derivative, have been determined.[115]

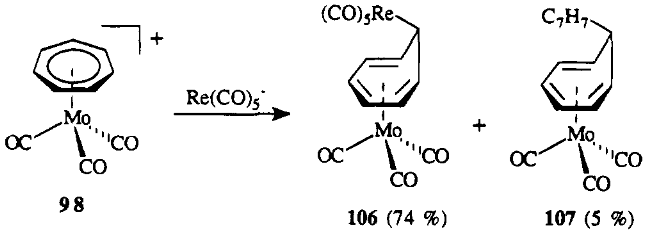
Treatment of $[\mathrm{Cr}(\eta^7\text{-}\mathrm{C_7H_7})(\mathrm{CO})_3]^+$ (**97**) with dppm (or dppe) in acetone at room temperature gives the *exo*-adduct **102**. ^{31}P NMR data confirm the presence of a ring-bonded phosphorus (δ +20.8) and a pendant phosphorus (δ −27.8). Upon heating, compound **102** (n = 1) converts into a mixture of carbonyl substituted product **103** and ring substituted product **104**. Interestingly, the reaction of **97** with $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{THF})]^+$ and $\mathrm{Ph_2P(CH_2)_3PPh_2}$ affords the diphosphine bridged dication **105** (Scheme 47).[116]

Recently, the addition of a variety of functionalized zinc−copper reagents RCu(CN)ZnI [R = $(\mathrm{CH_2})_n\mathrm{CO_2Et}$ (n = 2−4), $(\mathrm{CH_2})_n\mathrm{CN}$ (n = 2−4), $\mathrm{CH_2Ph}$, or $\mathrm{CH_2CH{=}CH_2}$] to **97** has been reported. The reactions give high yields of η^6-cycloheptatriene complexes with a functionalized side chain at the C7 position of the ring. Upon treatment with lithium diisopropylamide,

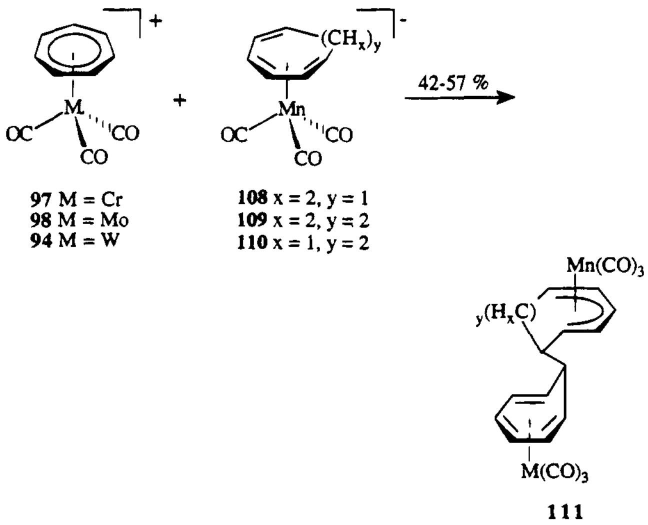
Scheme 47



Scheme 48

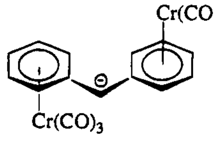


Scheme 49

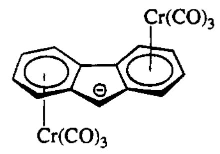


the ester-substituted adducts undergo intramolecular cyclization generating fused bicyclo[5.3.0]decane and -[5.4.0]undecane derivatives.[117]

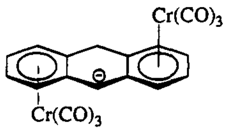
The addition of organometallic nucleophiles to **97**, **98**, and **94** has also been reported. Treatment of **98** with $[Re(CO)_5]^-$ gives the expected adduct **106** with small amount of **107** (Scheme 48). Both of these complexes have been structurally characterized.[118] The addition of dianions $[M'(CO)_4]^{2-}$ (M′ = Os or Ru) to **97** or **98** leads to the heterotrimetallic complexes *cis*-$M'(CO)_4[M(\mu\text{-}\eta^1{:}\eta^6\text{-}C_7H_7)(CO)_3]_2$. For the complex with M = Mo, M′ = Os, the crystal structure has been determined.[119] The reaction of **97**, **98**, and **94** with $[Mn(\eta^4\text{-}C_7H_8)(CO)_3]^-$ (**108**), $[Mn(\eta^4\text{-}C_8H_{10})(CO)_3]^-$ (**109**), or $[Mn(\eta^4\text{-}C_8H_8)(CO)_3]^-$ (**110**) results in coupling of the ring ligands, giving the hydrocarbon-bridged complexes **111** (Scheme 49).[120] Other nucleophiles, such as **112**–**116**, also attack the C_7 ring of **97**, **98**, and **94** forming the *exo*-isomer of the adducts.[121,122]



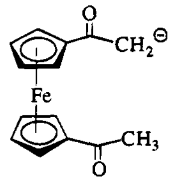
112



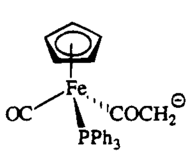
113



114



115



116

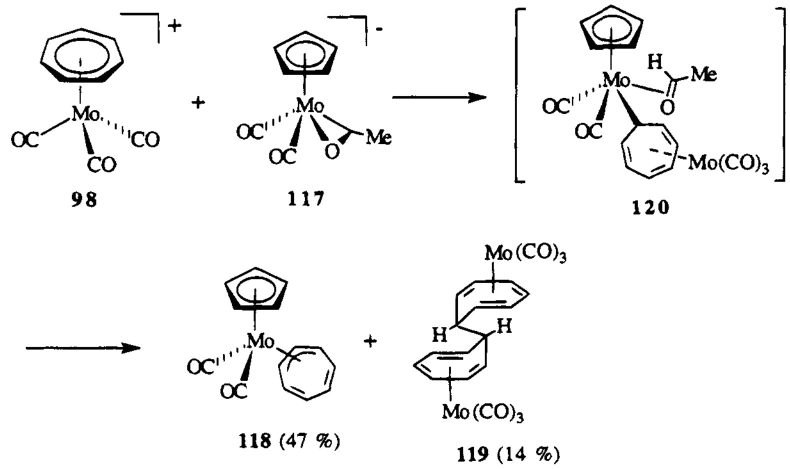
Treatment of **98** with the complexed acetaldehyde anion **117** gives a mixture of products from which **118** and **119** can be isolated. The formation of **118** may arise from the intermediate **120** formed by nucleophilic attack of the anion **117** at the C_7 ring of **98**. As the η^3-tropyl interaction is formed, the aldehyde and $Mo(CO)_3$ fragments are lost in **120** leading to **118** (Scheme 50).[123]

3. Lewis Base Addition and Ring Slippage Reactions

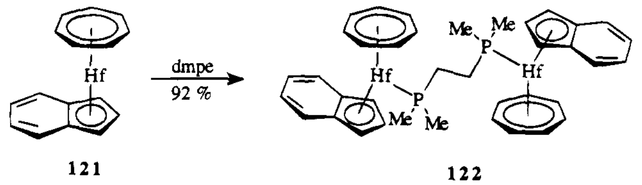
The coordinatively unsaturated mixed-sandwich compounds $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_9H_7)$ [M = Zr (**66**) or Hf (**121**)], upon treatment with PMe_3, are transformed into the 18-electron complexes $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_9H_7)(PMe_3)$. With the bidentate dmpe, the hafnium complex **121** converts into the bridged dimer **122** of which the crystal structure has been determined (Scheme 51).[28]

Addition of Lewis bases to coordinatively saturated complexes may induce a hapticity change of the C_7 ring. Thus the complexes $M(\eta^7\text{-}C_7H_7)(CO)_2X$ (M = Mo or W; X = Cl or I) **123-126** react with bidentate ligands, such as dppe, dppm, or en giving the trihapto

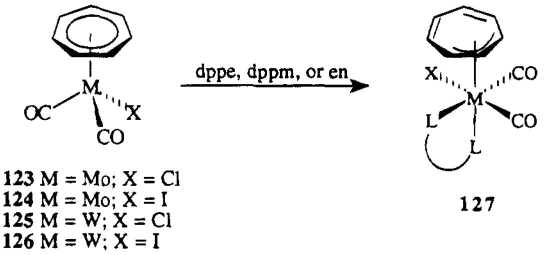
Scheme 50



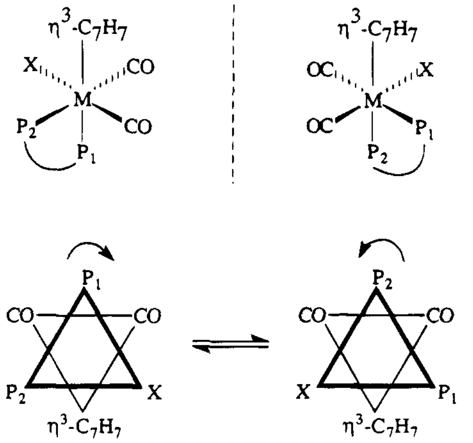
Scheme 51



Scheme 52



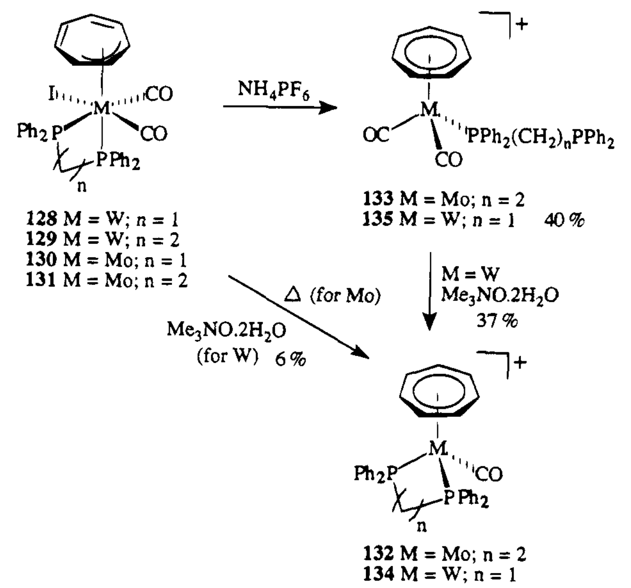
Scheme 53



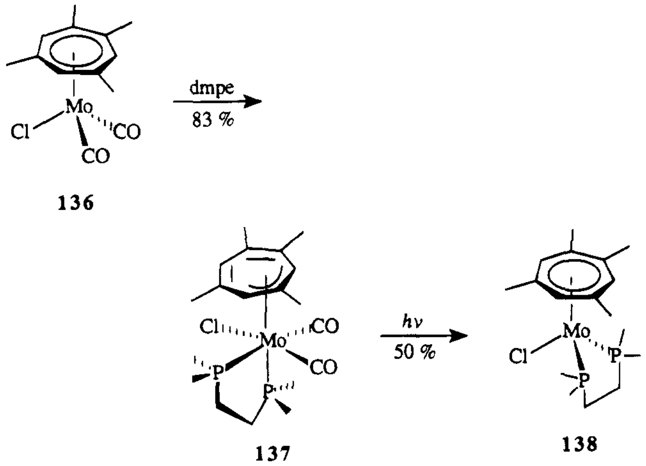
complexes **127** (Scheme 52).[124-126] All of these compounds undergo 1,2-shift of metal around the C_7 ring, so only one ^1H NMR resonance is observed for the C_7 ring protons. For the en complexes, this 1,2-shift process can be frozen out at low temperature and the individual environments of the η^3-C_7H_7 ring can be resolved. The dppe complexes also exhibit a fluxional process which interconverts inequivalent phosphorus environments. A trigonal twist rearrangement has been proposed for this process (Scheme 53).[126] The diene moiety in the η^3-C_7H_7 ligand of the tungsten complexes $W(\eta^3\text{-}C_7H_7)(CO)_2(L\text{-}L)I$ [L-L = dppm (**128**) or dppe (**129**)] undergoes a Diels–Alder reaction with TCNE forming the corresponding adducts.[126]

The tungsten complexes **128** and **129** are more stable than the molybdenum analogs **130** and **131** with respect to loss of CO and conversion to η^7-cycloheptatrienyl derivatives.[124,125] Thus, while compound **131** converts to **132** readily in refluxing benzene, the tungsten compound **129** is stable even in refluxing toluene. Similarly, treatment of **131** with an excess of NH_4PF_6 gives the η^1-dppe complex **133**, but the tungsten analog **129** remains intact under these conditions. However, compound **128**, with a strained four-membered metal chelate ring, does react slowly with $Me_3NO{\cdot}2H_2O$ to give **134**, and with NH_4PF_6 to give **135**. The former compound is better prepared by treating the latter compound with $Me_3NO{\cdot}2H_2O$ (Scheme 54).

Scheme 54



Scheme 55

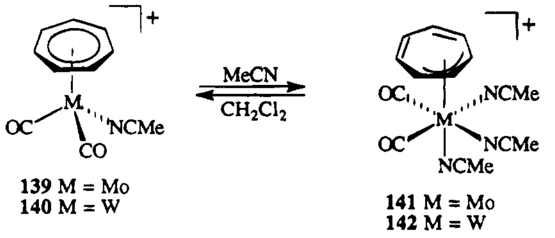


The tetramethylcycloheptatrienyl molybdenum complex $Mo(\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6)(CO)_2Cl$ (**136**) reacts with dmpe in a similar manner giving the trihapto complex **137**. Variable-temperature NMR studies have shown that this complex is fluxional due to trigonal twist rearrangement and 1,2-shift of metal around the C_7 ring. The value of $\Delta G^{\ddagger}$ for the former process has been estimated to be 53.3 kJ/mol. Upon photolysis, displacement of CO ligands occurs with the formation of η^7-cycloheptatrienyl complex **138** (Scheme 55).[12]

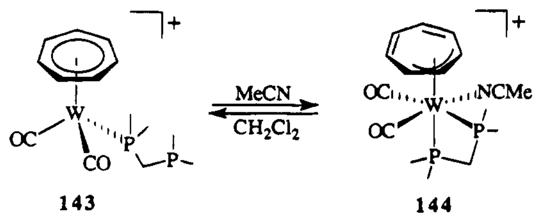
The cations $[M(\eta^7\text{-}C_7H_7)(CO)_2(MeCN)]^+$ [M = Mo (**139**) or W (**140**)] also undergo hapticity change in acetonitrile solution giving the trisacetonitrile complexes **141** and **142**, which are the first examples of a cationic η^3-C_7H_7 species. In weak coordinating solvents, such as dichloromethane and THF, displacement of two acetonitrile ligands from **141** and **142** is accompanied by reversion to a heptahapto-bonded cycloheptatrienyl ring (Scheme 56).[108,127] The interconversion of related complexes **143** and **144** has also been established (Scheme 57).[108]

The analogous cationic carbonylisonitrile complexes **145** and **146** also undergo η^7-η^3 ring slippage on addition of $CNBu^t$. However, the reversion of

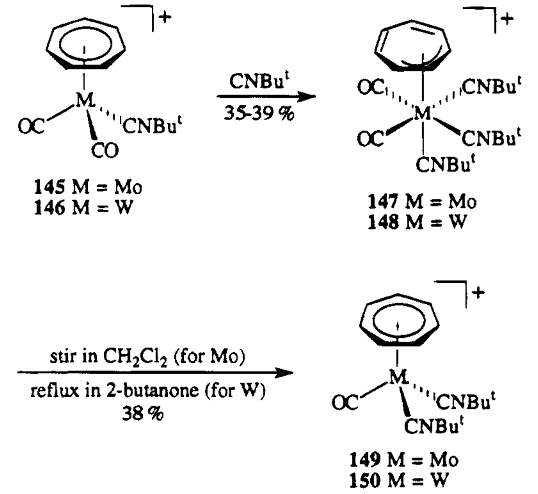
Scheme 56



Scheme 57



Scheme 58

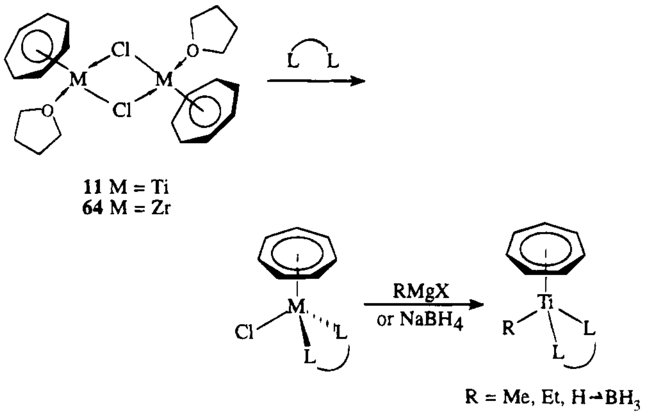


trihapto complexes **147** and **148** to products with a heptahapto-bonded C_7 ring involves loss of one CNBu^t ligand and one CO ligand (Scheme 58), which is in contrast to the case of acetonitrile analogs.[128] Compounds **149** and **150** are the formal substitution products of **145** and **146** with CNBu^t, thus the reaction sequence shown in Scheme 58 provides a well-defined example of ligand substitution at the metal center of cyloheptatrienyl complexes proceeding via an η^3-C_7H_7 intermediate. In an excess of CNBu^t, the molybdenum compound **149** undergoes further ring slip giving $[Mo(\eta^3\text{-}C_7H_7)(CO)(CNBu^t)_4]^+$, which upon heating, converts to a mixture of **149** and the substituted product $[Mo(\eta^7\text{-}C_7H_7)(CNBu^t)_3]^+$.[128]

4. Ligand Exchange Reactions

The readily accessible binuclear compounds $[M(\eta^7\text{-}C_7H_7)(THF)(\mu\text{-}Cl)]_2$ [M = Ti (**11**) or Zr (**64**)] are good precursors toward cycloheptatrienyl derivatives of titanium and zirconium. They undergo bridge-splitting reactions upon treatment with a wide range of O-, N-, and P-donor ligands, such as dme, tmeda, PMe_3, dmpe, dppe, dippe, and *trans*-1,2-bis(dimethylphosphino)cyclopentane, forming the monomeric species $M(\eta^7\text{-}C_7H_7)(L\text{-}L)Cl$. Reaction of alkyl Grignard reagents or $NaBH_4$ with the appropriate titanium chloro derivatives gives the corresponding alkylated or single bridging $M{-}H{\rightharpoonup}BH_3$ compounds (Scheme 59).[22,24] The THF ligands in $Zr(\eta^7\text{-}C_7H_7)(THF)_2I$ (**63**) can also be displaced by PMe_3 giving the complex $Zr(\eta^7\text{-}C_7H_7)(PMe_3)_2I$.[26b,27]

Scheme 59



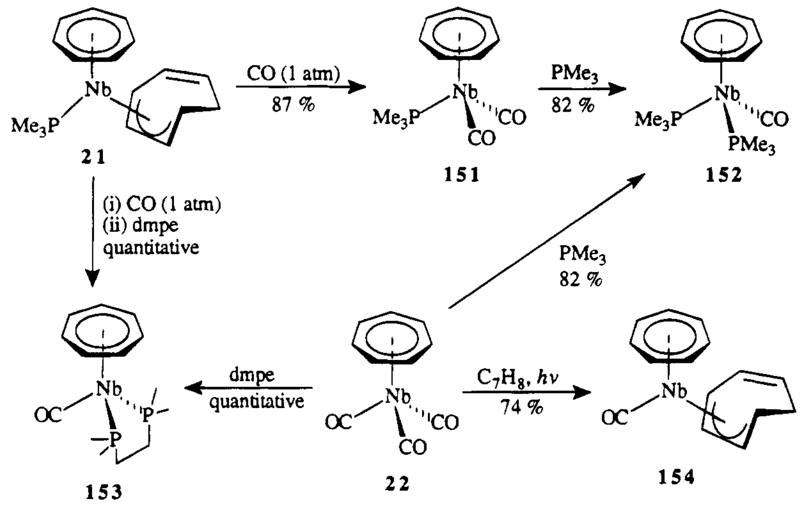
The η^4-C_7H_8 ligand in niobium complex $Nb(\eta^7\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)$ (**21**) is labile and can be replaced by CO ligands. The resulting complex **151** undergoes further substitution with PMe_3 and dmpe. The former reaction gives bis(trimethylphosphine) product **152** while the latter reaction leads to substitution of CO and PMe_3 forming **153**. The compounds **152** and **153** can also be prepared by treating the tricarbonyl complex $Nb(\eta^7\text{-}C_7H_7)(CO)_3$ (**22**) with the corresponding phosphines. Under photolysis, **22** reacts with an excess of cycloheptatriene affording **154** (Scheme 60).[35] This is analogous with the photochemical reaction of $Nb(\eta^5\text{-}C_5H_5)(CO)_4$ in the presence of cycloheptatriene, which gives $Nb(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_7H_8)(CO)_2$.[129]

The η^7-C_7H_7 group normally acts as a robust, nonlabile ligand. However, displacement of C_7 ring in cycloheptatrienyl complexes has been reported. Treatment of $Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ (**80**) with dithioacetic acid gives $Ti(\eta^5\text{-}C_5H_5)(S_2CCH_3)_3$ (**155**), while similar reaction on $Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ (**71**) affords $Nb(\eta^5\text{-}C_5H_5)(S_2CCH_3)_2(\eta^2\text{-}S_2)$ (**156**) (Scheme 61). The crystal structures of both of these seven-coordinate molecules have been reported.[38] The reaction of **80** with trifluoroacetic acid, however, leads to the formation of trifluoroacetate bridged dimer $[Ti(\eta^5\text{-}C_5H_5)]_2(\mu\text{-}CF_3CO_2)_4$ in 65% yield.[130]

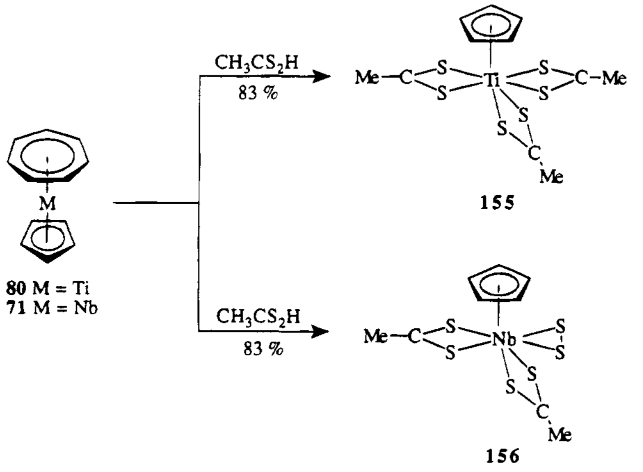
The reaction of $[M(\eta^7\text{-}C_7H_7)(CO)_3]^+$ [M = Cr (**97**), Mo (**98**), or W (**94**)] with phosphines leads to nucleophilic attack on the ring,[131] substitution of CO ligand,[109,132] or displacement of the ring[133] depending on the reaction conditions, the nature of the nucleophile and the metal center. With excess PPh_3, the tungsten cation **94** is transformed into *fac*-$W(PPh_3)_3(CO)_3$. Kinetic studies have showed that the reaction involves rapid preequilibrium formation of a π-complex, followed by rate-determining attack by a second PPh_3 molecule at the metal. Subsequent attack by a third PPh_3 at the metal results in rapid displacement of the C_7 ring to give the product.[134] Treatment of **98** or **94** with the η^1-dppe molybdenum complex $[Mo(\eta^7\text{-}C_7H_7)(CO)_2(\eta^1\text{-dppe})]^+$ (**133**) results in CO substitution yielding the dppe-bridged dications $[M(\eta^7\text{-}C_7H_7)(CO)_2(\mu\text{-dppe})Mo(\eta^7\text{-}C_7H_7)(CO)_2]^{2+}$.[125]

The complexes $M(\eta^7\text{-}C_7H_7)(CO)_2X$ (M = Mo or W, X = halide) are key compounds in generating other

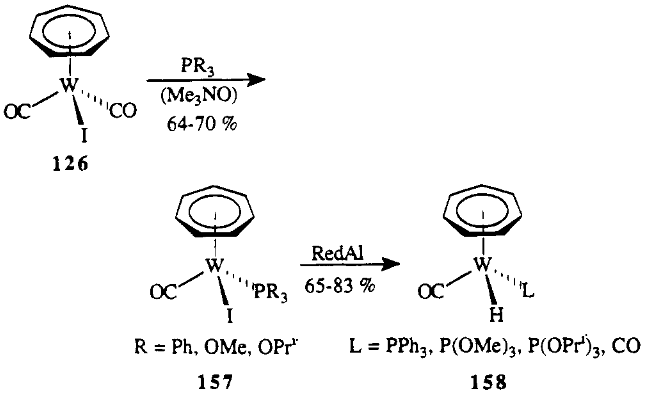
Scheme 60



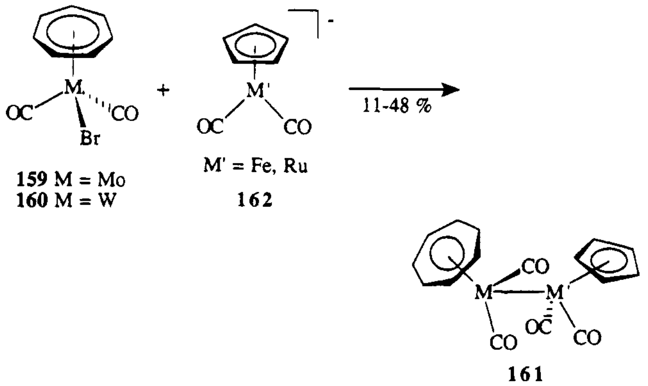
Scheme 61



Scheme 62



Scheme 63



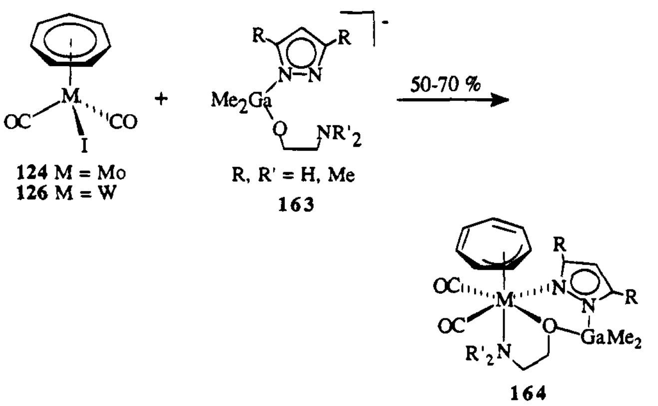
cycloheptatrienyl molybdenum and tungsten complexes. They undergo halide and/or CO substitution with a variety of reagents. For example, treatment of W(η^7-C_7H_7)$(CO)_2I$ (**126**) with PPh_3 gives the monosubstituted product **157** (R = Ph).[135] For the reaction with phosphites $P(OMe)_3$ and $P(OPr^i)_3$, compound Me_3NO is also added for decarbonylation.[43] Both **126** and **157** react with sodium dihydridobis(2-methoxyethoxy)aluminum (RedAl) to give the corresponding tungsten hydride complexes **158** (Scheme 62). The tetramethylcycloheptatrienyl analogs W(η^7-$C_7H_3Me_4$-1,2,4,6)$(CO)_2X$ (X = Br or I), prepared from the reaction of tricarbonyl cation [W(η^7-$C_7H_3Me_4$-1,2,4,6)$(CO)_3]^+$ and $[Bu_4N][X]$, react with the phosphorus-donor ligands and sequence RedAl in a similar manner.[43]

The molybdenum complex Mo(η^7-C_7H_7)$(CO)_2Br$ (**159**) also reacts with PR_3 (R = Me or Ph) to give the CO substitution products Mo(η^7-C_7H_7)(CO)$(PR_3)Br$, which, upon treatment with appropriate organolithium or Grignard reagents, generate Mo(η^7-C_7H_7)(CO)$(PR_3)R'$ (R' = Me, Ph, C_6F_5, CH=CH_2, C≡CPh, or C≡CBu^t).[136]

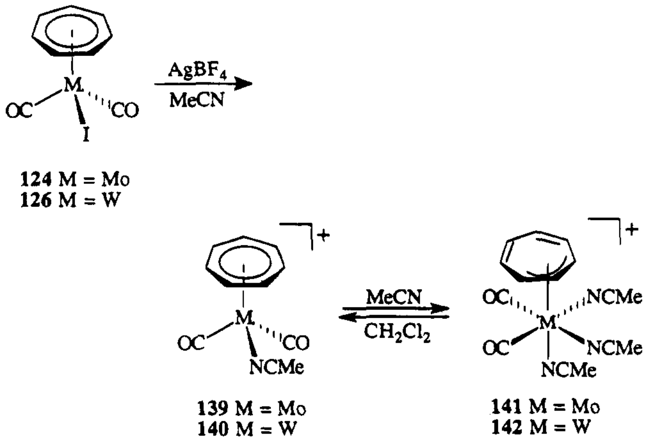
Displacement of halide in M(η^7-C_7H_7)$(CO)_2X$ (M = Mo or W; X = halide) with nucleophiles is well-documented.[137] For example, reaction of **159** with RLi (R = Me or Ph) gives the products Mo(η^7-C_7H_7)$(CO)_2R$, which undergo SO_2 insertion into the Mo−C(R) bond. For R = Me, insertion of SeO_2, TeO_2, and Zn was also observed.[138]

Recently, the heterobimetallic complexes M(η^7-C_7H_7)$(CO)_2$M'(η^5-C_5H_5)$(CO)_2$ (M = Mo or W; M' = Fe or Ru) (**161**) have been prepared by treating **159** or **160** with [Na][M'(η^5-C_5H_5)$(CO)_2$] (**162**) (Scheme 63).[139] The molecular structure of **161** (M = Mo; M' = Ru) reveals an unsupported Mo−Ru bond and a *cis* arrangement of C_5 and C_7 rings. However, solution infrared studies show that the conformation is solvent-dependent. In addition, the ambient-temperature ^{13}C NMR spectra of **161** display only a single resonance for the carbonyl carbons. This observation has been attributed to an intermetallic carbonyl scrambling process. The reaction of **159** with [K][Ru(η^5-C_5Me_5)$(CO)_2$] gives the metal−metal bonded complex in very

Scheme 64



Scheme 65



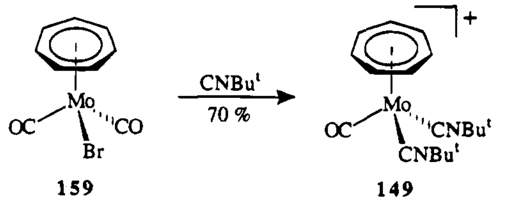
low yield together with the unexpected, but structurally characterized, $Mo(CO)_3(\mu\text{-}\eta^6,\eta^1\text{-}C_7H_7)Ru(\eta^5\text{-}C_5Me_5)(CO)_2$ as the major product.[139]

Treatment of **124** or **126** with the novel ligands **163** results in displacement of iodide together with a η^7-η^3 hapticity change. The products **164** are pseudo octahedral with the organogallate ligands occupying a set of facial positions and the η^3-C_7H_7 ring situated opposite to the nitrogen atom (Scheme 64).[140] This has been confirmed by the X-ray crystal structure of **164** (M = Mo; R = Me; R′ = H).[141]

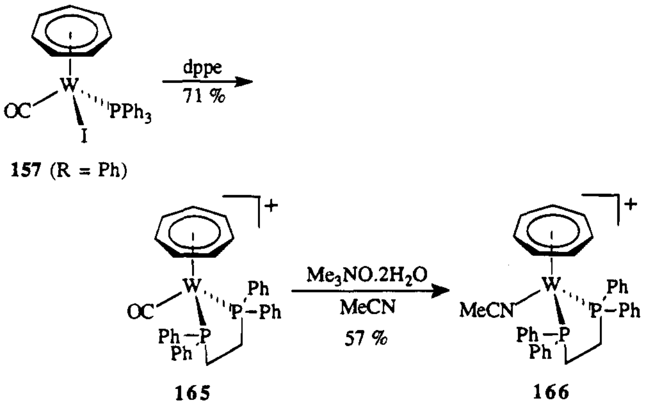
Reaction of **126** with $AgBF_4$ in acetonitrile gives the trihaptocycloheptatrienyl complex **142**, which in CH_2Cl_2 is converted into **140**. As mentioned in section VI.B.3, dissolution of **140** in acetonitrile results in rapid reformation of **142**, indicating that **140** is the actual first product in this reaction. A similar reaction sequence has been observed for the molybdenum complex **124** but an equilibrium mixture of **139** and **141** is produced. Removal of acetonitrile and dissolution of the residue in CH_2Cl_2 gives **139** as the sole product (Scheme 65). The benzonitrile analog $[Mo(\eta^7\text{-}C_7H_7)(CO)_2(NCPh)]^+$ has also been prepared similarly.[108,127] Two of the acetonitrile ligands in **141** and **142** can be displaced by dppe giving $[M(\eta^3\text{-}C_7H_7)(CO)_2(dppe)(MeCN)]^+$ (M = Mo or W).[108,127]

Displacement of halide in $M(\eta^7\text{-}C_7H_7)(CO)_2X$ (M = Mo or W; X = halide) may also accompany CO substitution. For example, treatment of **159** with 2 equiv of $CNBu^t$ gives **149** in high yield (Scheme 66).[128] Similarly, the compound **157** (R = Ph), upon treatment with dppe, is converted into the cation **165**. Further reaction with $Me_3NO{\cdot}2H_2O$ in refluxing acetonitrile leads to CO substitution forming the complex **166** (Scheme 67).[135]

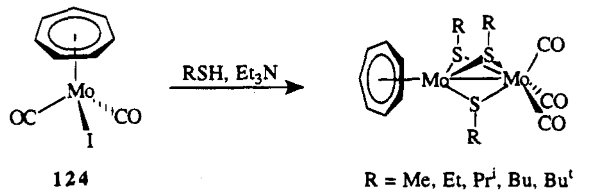
Scheme 66



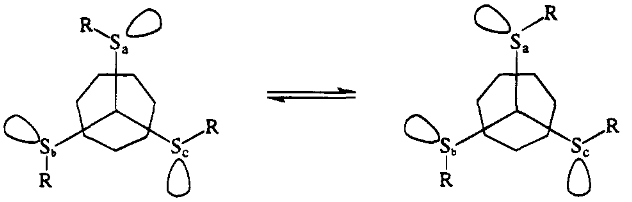
Scheme 67



Scheme 68

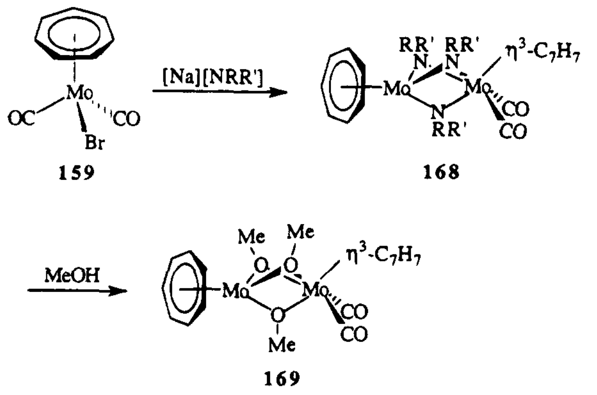


Scheme 69

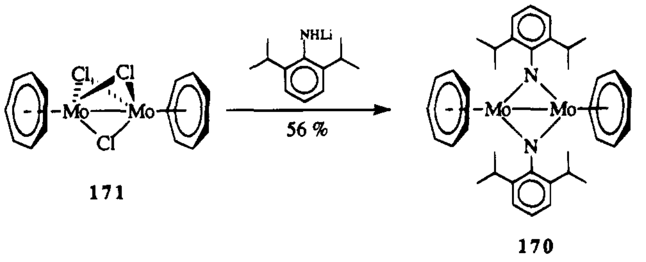


Treatment of **124** with thiols RSH (R = Me, Et, Pr^i, Bu, or Bu^t) in the presence of triethylamine produces a series of unsymmetric thiolato-bridged complexes $Mo(\eta^7\text{-}C_7H_7)(\mu\text{-}SR)_3Mo(CO)_3$ (**167**) (Scheme 68).[142,143] Infrared and variable-temperature NMR spectroscopy reveal that the complexes exist as two isomers differing in the relative orientations of the R groups on bridging sulfur (Scheme 69). These isomers interconvert rapidly at ambient temperature, attributed to a low-energy sulfur inversion process.[143] The monosubstituted derivatives $Mo(\eta^7\text{-}C_7H_7)(\mu\text{-}SBu^t)_3Mo(CO)_2L$ [L = $P(OMe)_3$, $PMePh_2$, PMe_2Ph, or PMe_3], prepared from the reaction of **167** (R = Bu^t) and the corresponding phosphorus donors, also exhibit such fluxional process and the free energies of activation for sulfur inversion have been estimated ranging from 46.7 to 58.8 kJ/mol. The selenium analogs of **167** have also been prepared similarly[142]

Scheme 70



Scheme 71



and the X-ray structure of Mo(η^7-C_7H_7)(μ-SePh)$_3$Mo(CO)$_3$ has been determined.[144]

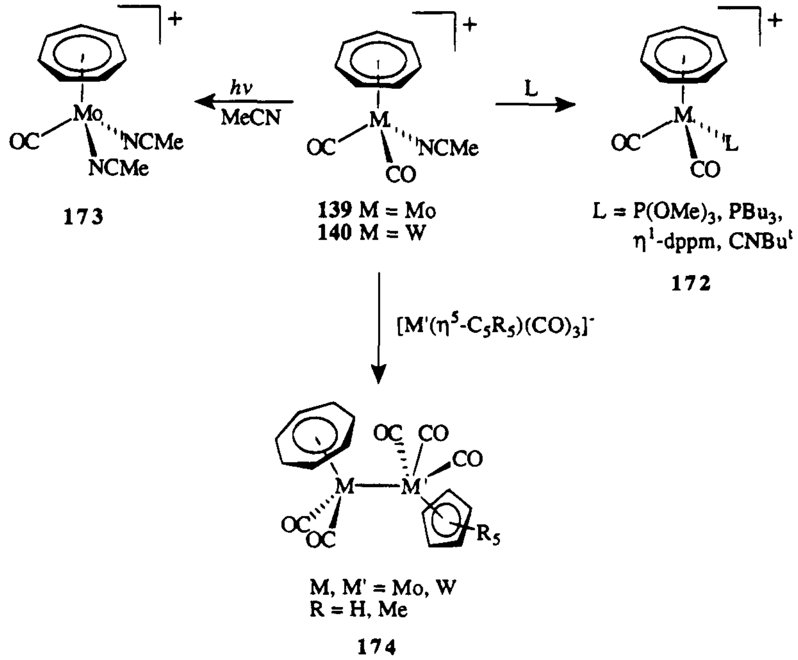
The triply amido-bridged molybdenum compounds Mo(η^3-C_7H_7)(CO)$_2$(μ-NRR')$_3$Mo(η^7-C_7H_7) (NRR' = NH_2, NC_4H_4, NHPh, or $NHC_6H_4NO_2$) (**168**) can be synthesized, in low yields, by treating Mo(η^7-C_7H_7)(CO)$_2$Br (**159**) with the corresponding amides. For NRR' = NH_2, it is much more convenient to prepare from Mo(η^7-C_7H_7)(CO)$_2$Me in liquid ammonia. These amido compounds react with MeOH forming the bridging methoxy compounds **169** (Scheme 70).[145] The related bridging-imido complex **170** has recently been reported.[146] The synthesis involves treatment of **171** with ArNHLi (Scheme 71).

Whiteley *et al.* have demonstrated that the cations **139** and **140** are useful precursors to other cycloheptatrienyl derivatives of molybdenum and tungsten. As shown in Scheme 72, the acetonitrile ligand of these cations is labile and can be displaced readily by various donors, such as PR_3 (R = OMe or Bu), dppm, and CNBu^t, forming the monosubstituted products **172**.[108,128] Photolysis of the molybdenum complex **139** in acetonitrile leads to CO substitution giving the bisacetonitrile cation **173**.[108,127] A series of metal–metal-bonded complexes M(η^7-C_7H_7)(CO)$_2$M'(η^5-C_5R_5)(CO)$_3$ (M, M' = Mo or W; R = H or Me) (**174**) have also been prepared from **139** and **140** and the appropriate anions [M'(η^5-C_5R_5)(CO)$_3$]$^-$.[127,147] The molecular structure of **174** (M = M' = Mo; R = H) shows an unsupported metal–metal bond and a *trans* arrangement of the C_5 and C_7 rings.[148]

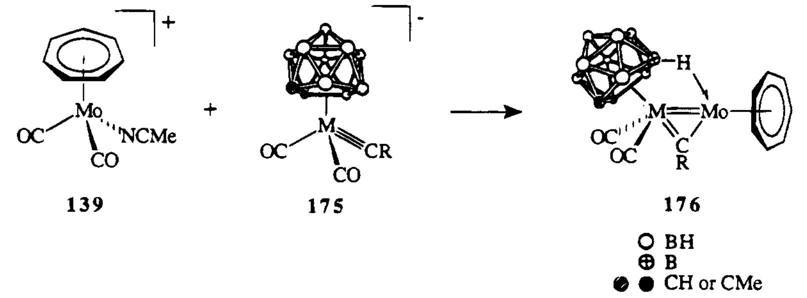
The molybdenum complex **139** has also been employed by Stone *et al.* to react with the carbaborane metal carbynes **175**.[149] The reactions give the bimetallic complexes Mo(η^7-C_7H_7)(μ-CR)M(η^5-$C_2B_9H_9R^1R^2$)(CO)$_2$ (M = Mo or W; R = C_6H_4Me-4, C_6H_4Me-2, or C≡CBu^t; R^1, R^2 = H or Me) (**176**), which have a metal–metal bond bridged by an alkylidyne group and a B—H→Mo agostic bond (Scheme 73). The related complex Mo(η^7-C_7H_7)(μ-CC$_6H_4$Me-4)W(η^6-$C_2B_{10}H_{10}Me_2$)(CO)$_2$ has also been synthesized from **139** and [NEt$_4$][W(η^6-$C_2B_{10}H_{10}Me_2$)(CO)$_2$(≡CC$_6H_4$Me-4)].

While treatment of **176** (M = W; R = C_6H_4Me-4; R^1 = R^2 = Me) with PMe_3 displaces one of the CO ligands,[149] the reaction of **176** (M = W; R = C_6H_4Me-4; R^1 = H; R^2 = H or Me) and $PHPh_2$ produces the complexes **177**, which have an unusual structure established by X-ray crystallography (Scheme 74).[150] Presumably, addition of $PHPh_2$ leads to attack of CO on the μ-alkylidyne fragment, giving the intermediate **178**. A metal-assisted hydrogen transfer from the coordinated $PHPh_2$ molecule to the ketenyl oxygen atom, accompanied with migration of the resulting

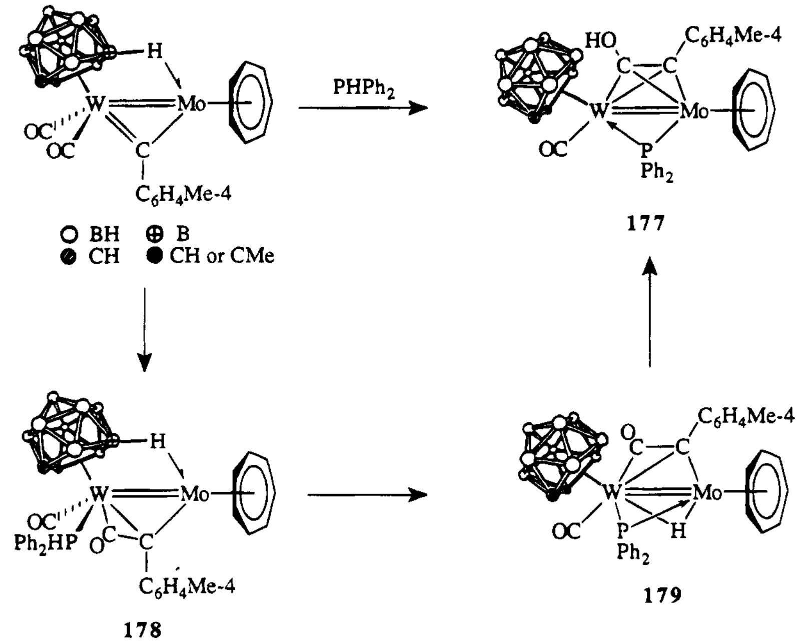
Scheme 72



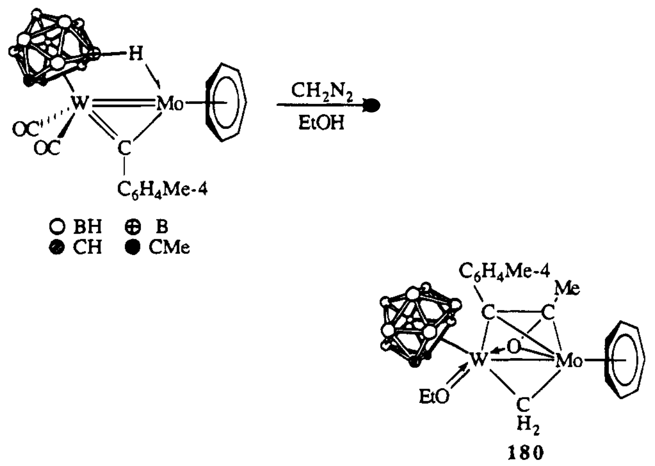
Scheme 73



Scheme 74



Scheme 75



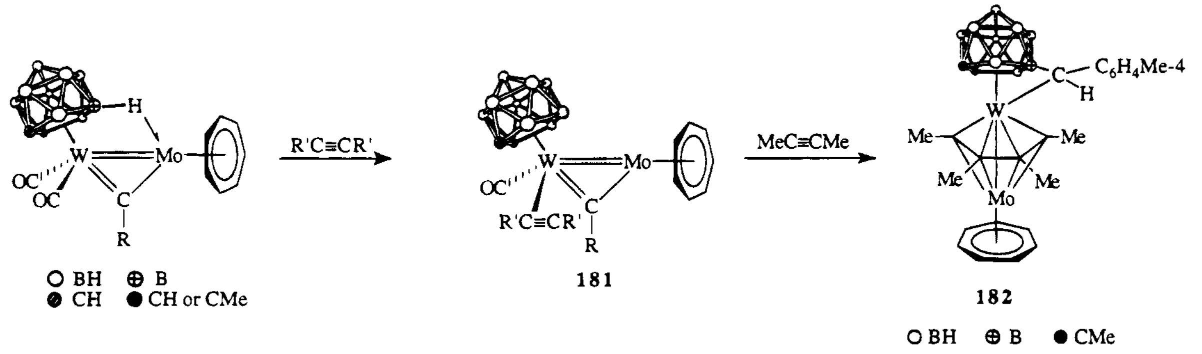
phosphido ligand into the bridging position via intermediate **179**, could lead to the product **177**.

The complex **176** (M = W; R = C_6H_4Me-4; R^1 = H; R^2 = Me) also reacts with diazomethane in ether containing ethanol to give the methylene bridged complex **180**, of which the structure has been determined and the plausible mechanism of formation has been proposed (Scheme 75).[151]

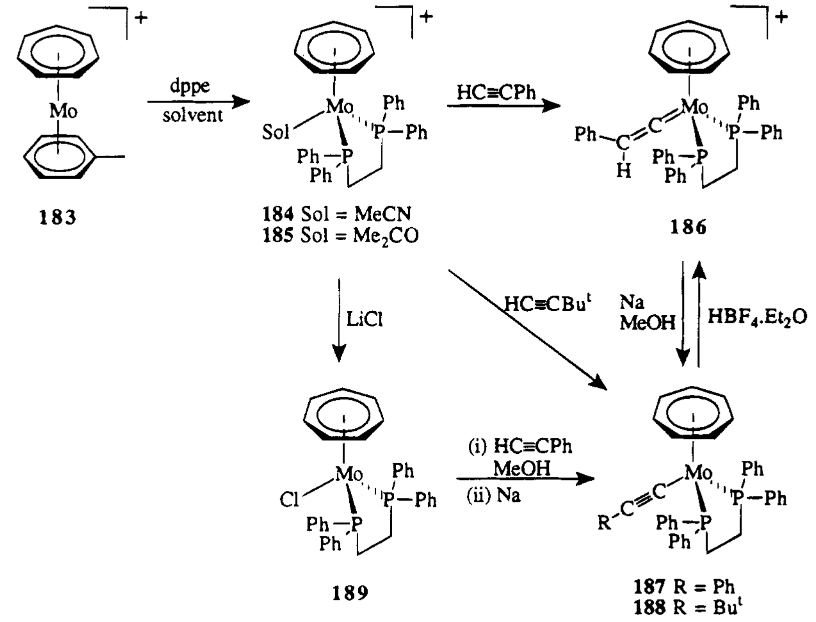
The reaction of **176** and alkynes has also been studied.[152] The complexes **176** (M = W; R = C_6H_4-Me-4 or C≡CBu^t; R^1 = Me; R^2 = H or Me) react with R′C≡CR′ (R′ = Me, Et, or Ph) to give the substituted products **181** in which the agostic bond is absent. Treatment of **181** (R = C_6H_4Me-4; R′ = Me) with MeC≡CMe at higher temperature (100 °C) leads to the novel compound **182** (Scheme 76). The X-ray crystal structure shows that the Mo–W bond is symmetrically bridged by a μ-η^4-C_4Me_4 fragment and the tungsten atom is ligated by a CH(C_6H_4Me-4)-$C_2B_9H_8Me_2$ moiety.

The mixed-sandwich cation [Mo(η^7-C_7H_7)(η^6-C_6H_5-Me)]$^+$ (**183**), which can be prepared by either treating [Mo(η^6-C_6H_5Me)(η^3-C_3H_5)Cl]$_2$ with $(AlEtCl_2)_2$ in the presence of cycloheptatriene[153] or refluxing [Mo(η^7-C_7H_7)(CO)$_3$]$^+$ (**98**) in toluene,[154] is an excellent precursor to cycloheptatrienyl molybdenum derivatives.[154-157] Recently, the synthetic utility of this compound has been extended. For example, treatment of **183** with 1 equiv of dppe in acetonitrile or acetone causes displacement of the toluene ligand giving [Mo(η^7-C_7H_7)(dppe)(solvent)]$^+$ [solvent = MeCN (**184**) or acetone (**185**)].[157] These complexes react with HC≡CPh forming the phenylvinylidene complex **186**, which is readily deprotonated to give the alkynyl complex **187**. By contrast, the reaction of **185** with HC≡CBu^t affords the corresponding alkynyl complex **188** directly. Alternatively, the compound Mo(η^7-C_7H_7)(dppe)Cl (**189**), which is readily available from **185** and LiCl, reacts with HC≡CPh in refluxing methanol followed by the addition of sodium, giving

Scheme 76



Scheme 77

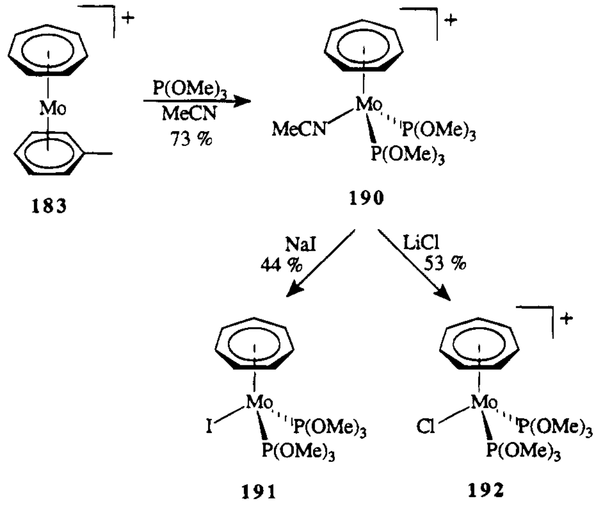


187 in moderate yield. Upon protonation with $HBF_4{\cdot}Et_2O$, compound **187** regenerates **186** (Scheme 77).[158] Similarly, the compound $Mo(\eta^7\text{-}C_7H_7)(CO)(PMe_3)(C{\equiv}CPh)$ can also be protonated to give the carbene $[Mo(\eta^7\text{-}C_7H_7)(CO)(PMe_3)(C{=}CHPh)]^+$ in 64% yield.[136] The analogous dicarbonylalkynyl complexes $M(\eta^7\text{-}C_7H_7)(CO)_2(C{\equiv}CPh)$ (M = Mo or W) have also been prepared by treating $Mo(\eta^7\text{-}C_7H_7)(CO)_2I$ (**124**) or $W(\eta^7\text{-}C_7H_7)(CO)_2Cl$ (**125**) with $LiC{\equiv}CPh$.[158b]

Heating **183** in acetonitrile with 2 equiv of $P(OMe)_3$, instead of 1 equiv of dppe, affords the related cation $\{Mo(\eta^7\text{-}C_7H_7)[P(OMe)_3]_2(MeCN)\}^+$ (**190**). This reacts with NaI giving the neutral compound **191**. However, reaction with LiCl produces the paramagnetic cation **192** (Scheme 78).[135]

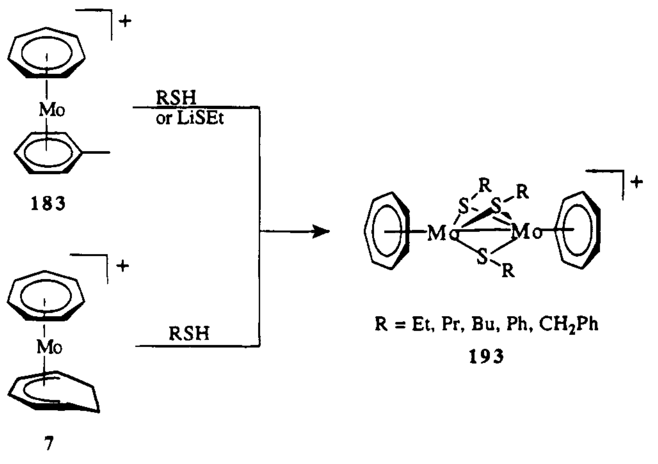
The reaction of **183** with thiols has also been studied.[159] The reactions give a new series of binuclear thiolato-bridged molybdenum complexes $[Mo_2(\eta^7\text{-}C_7H_7)_2(\mu\text{-}SR)_3]^+$ (R = Pr, Bu, Ph, or CH_2Ph) (**193**). The thioethoxyl analog $[Mo_2(\eta^7\text{-}C_7H_7)_2(\mu\text{-}SEt)_3]^+$ has also been prepared by treating **183** with LiSEt. An alternative route to these binuclear compounds is through the paramagnetic cation $[Mo(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]^+$ (**7**). Treatment of **7** with benzenethiol or phenylmethanethiol gives **193** (R = Ph or CH_2Ph) in good yields (Scheme 79). Dynamic NMR studies reveal that all of these complexes (except for R = Ph) are fluxional due to the inversion at the pyramidal sulfur center. The activation free energies of this process range from 52.9 to 58.1 kJ/mol and increase in the order R = CH_2Ph < Bu < Pr < Et.

Scheme 78

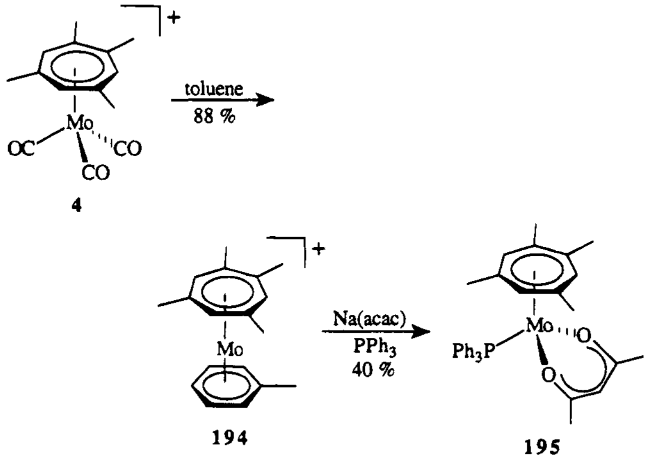


The tetramethyl-substituted analog of **183**, namely $[Mo(\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6)(\eta^6\text{-}C_6H_5Me)]^+$ (**194**), which can be prepared by refluxing $[Mo(\eta^7\text{-}C_7H_3Me_4\text{-}1,2,4,6)(CO)_3]^+$ (**4**) in toluene, shows diminished reactivity in comparison with **183**. Nevertheless, it reacts with benzenethiol producing the binuclear cation $[Mo_2(\eta^7\text{-}$

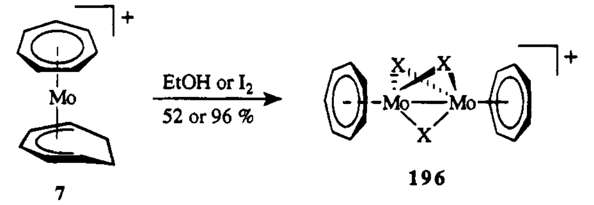
Scheme 79



Scheme 80



Scheme 81



$C_7H_3Me_4$-1,2,4,6)$_2$(μ-SPh)$_3$]$^+$ in excellent yield.[159] Upon treatment with sodium acetylacetonate [Na(acac)] and PPh_3, it converts into compound **195** (Scheme 80).[12]

The cation [Mo(η^7-C_7H_7)(η^5-C_7H_9)]$^+$ (**7**) also reacts with ethanol or iodine forming the dimeric species [Mo_2(η^7-C_7H_7)$_2$(μ-X)$_3$]$^+$ (X = OEt or I) (**196**) (Scheme 81).[41] These reactions, together with the reaction with thiols,[159] show the ease with which nucleophiles react with **7** to displace the η^5-C_7H_9 group. Indeed, solutions of this compound in halogenated solvents are unstable and decompose slowly.

The 17-electron compound Mo(η^7-C_7H_7)(MeCN)I_2 (**197**) undergoes ligand substitution reaction with PR_3 (R = Me or Ph) giving Mo(η^7-C_7H_7)(PR_3)I_2 [R = Me (**198**) or Ph (**199**)]. The former complex, upon further reaction with PMe_3, yields the salt [Mo(η^7-C_7H_7)(PMe_3)$_2$I][I] (**200**), whereas reaction with NaOMe produces **196** (X = OMe).[41] The acetonitrile ligand of **197** can also be displaced by weak anionic nucleophiles, such as iodide ion. Thus treatment of **197** with 1 equiv of [Bu_4N][I] gives [Bu_4N][Mo(η^7-C_7H_7)I_3] (**201**) of which the structure confirms a three-legged piano stool structure (Scheme 82).[41b] Displacement of acetonitrile ligand in analogous Mo(η^7-C_7H_7)(MeCN)Br_2[41] and W(η^7-C_7H_7)(MeCN)I_2[42] with Et_2S and PMe_3 occurs readily producing the complexes Mo(η^7-C_7H_7)(Et_2S)Br_2 and W(η^7-C_7H_7)(PMe_3)I_2 , respectively.

5. Redox Reactions

Sandwich compounds almost invariably undergo electron-transfer reactions and the electrochemistry of this class of compounds has been studied extensively. Table 1 summarizes the electrochemical data of M(η^7-C_7H_7)(η^5-C_5H_5) and their derivatives, obtained by cyclic voltammetry, as well as the gas-phase first vertical ionization potentials (IP) obtained by photoelectron spectroscopy. It is worth noting that, for the group 4 compounds, the influence of metal changes upon the ionization energies of the HOMO e_2 is evidently small.[161] However, the transition $e_2 \rightarrow a_1$, according to the UV–vis electronic absorption spectra, shifts to higher energy along the

Scheme 82

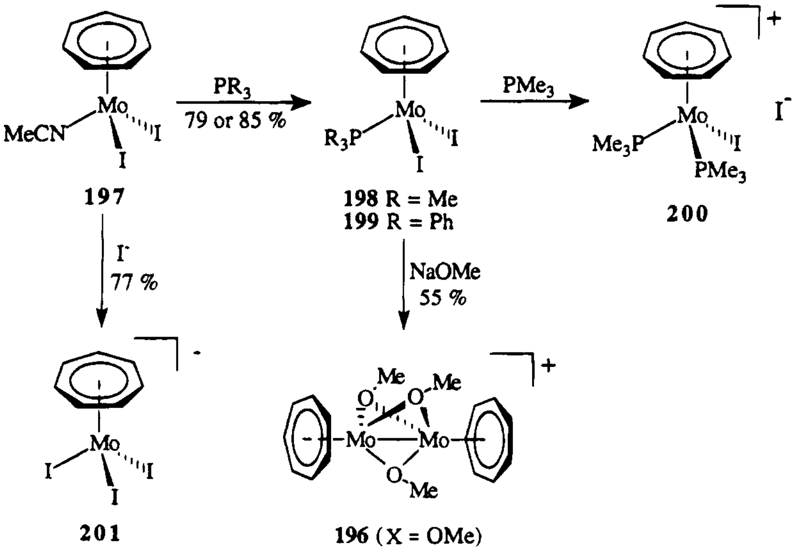


Table 1. Electrochemical Data of Sandwich Compounds $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5R_5)$ and Derivatives

compound	$E_{1/2}(0/+1)$ (V)[a]	$E_{1/2}(0/-1)$ (V)[a]	IP (eV)[b]	ref(s)
$Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$	+0.15[c]	−2.07[c]	6.86, 6.95, 6.83	160−162, 59
$Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)$			6.82	161
$Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5Me_5)$	+0.13[c]	−2.14[c]	6.70	160, 161
$Zr(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$			6.94	162
$Zr(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5Me_5)$			6.72	161
$Hf(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5Me_5)$			6.67	161
$V(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$	+0.19,[c] +0.26[d]	−2.55[d]	6.49, 6.42	37, 163, 59
$Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$	−0.82[c]	−2.40[e,f]	5.85, 5.98	37, 48b, 162
$Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)$	−0.82[c]	−2.40[e,f]		37, 48b
$Ta(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)$	−1.18[c]		5.47	37
$Cr(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$	−0.61[c]	−2.89[d,g]	5.59	163, 59
$Mo(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$	−0.60[c]		5.87, 5.70	41b, 162, 60
$Mo(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)$	−0.63[c]			41b
$Mo(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_9H_7)$	−0.48[c]			41b
$W(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$	−0.77[c]		5.58	42b, 164
$W(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)$	−0.79[c]		5.50	42b, 164
$W(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_9H_7)$	−0.66[c]			42b

[a] Half-wave potentials vs SCE; waves are reversible unless stated otherwise. [b] Gas-phase ionization potentials. [c] In MeCN. [d] In dme. [e] In THF. [f] Quasi-reversible. [g] Irreversible.

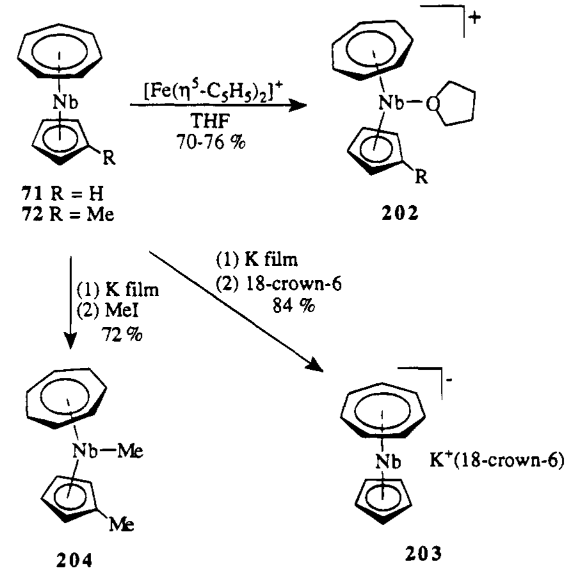
group which must be attributed to an increase in energy of the LUMO a_1.[32,161] A similar trend is not observed for the group 5 and 6 metal complexes.

The electrochemically generated $[Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]^-$ species has been characterized by EPR.[165] The room temperature spectrum shows an unpaired electron spin $S = 1/2$ interacting with proton nuclei of the C_5 and C_7 rings. The coupling due to ^{47}Ti and ^{49}Ti is also partially resolved. By deuteriating the cyclopentadienyl ligand, the EPR spectrum is significantly simplified and from these spectra, magnetic parameters can be determined as $g_{iso} = 1.986(9)$, $A_{iso}(C_5) = +4$ MHz, $A_{iso}(C_7) = +13$ MHz, and $A_{iso}(Ti) = 24$ MHz. The structure of the radical anion has also been determined by proton ENDOR at low temperature which shows that the geometry of the parent neutral molecule is preserved upon this one-electron reduction.[165]

Chemical oxidation and reduction of $Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4R)$ [(R = H (**71**) or Me (**72**)] have been reported.[37,48b] Treatment of these compounds with 1 equiv of $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ in THF gives the cations **202**, in which the THF ligand can be displaced with CO and PMe_3. The X-ray structure of **202** (R = Me) (Figure 3) confirms a bent sandwich structure with a coordinated THF ligand. In contrast, the 16-electron vanadium analog $[V(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]^+$ shows no tendency to form stable 18-electron adducts,[166] presumably because of the smaller atomic radius of vanadium. Reduction of **71** with a freshly prepared potassium film followed by the addition of 18-crown-6 affords the crystallographically characterized salt **203**. Similar treatment of **72** gives the corresponding anion which reacts with MeI to produce **204** in good yield (Scheme 83).[37]

The electrochemistry of $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ (M = V or Cr) has been examined and compared with the dibenzene analogs.[163] It has been shown that oxidation of the chromium species is easier than that of the vanadium counterparts and the symmetrical dibenzene complexes are oxidized preferentially to the mixed-ring analogs. Presumably, in the case of chromium complexes, an electron is removed from the doubly occupied HOMO a_1, thereby decreasing Coulomb repulsion, whereas for the vanadium complexes this HOMO is singly occupied and the electron is bound more tightly. The latter observation is a consequence of the higher electron-accepting properties of the ligand combination $C_5 + C_7$ ring compared to $C_6 + C_6$ ring. A linear correlation between the ionization potential (IP) and half-wave potential ($E_{1/2}$) has also been established and can be represented by the equation IP = $0.99E_{1/2} + 6.20$ eV.

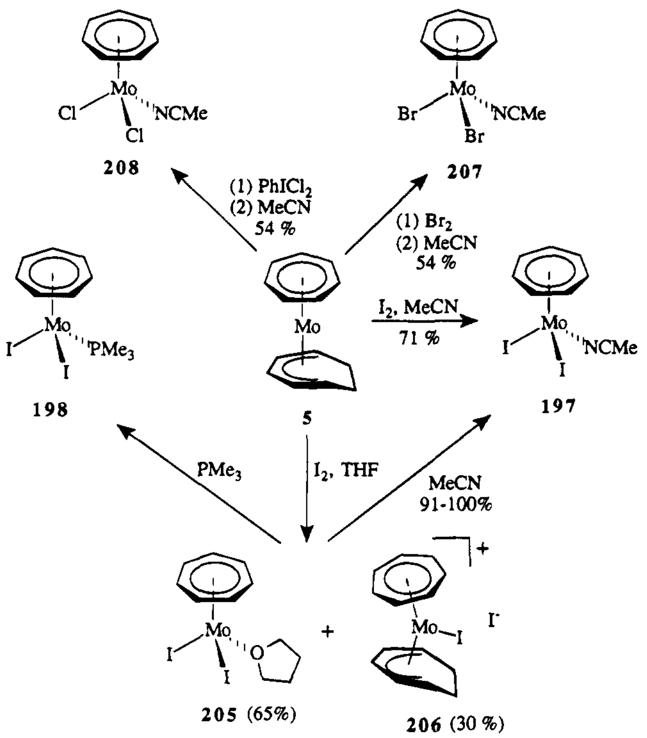
Scheme 83



The vapor-phase UV−vis absorption spectrum of $Cr(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ has been measured which shows surprisingly well-resolved Rydberg structure. The three Rydberg series converge to the same ionization limit 5.603 ± 0.007 eV, which is in good agreement with the values obtained by photoelectron spectroscopy.[167]

The sandwich compounds $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)$ (M = Mo or W) can be oxidized with iodine to give the corresponding cations.[168] Recently, several interesting charge-transfer complexes and intercalation compounds have been prepared by these species and their derivatives. Treatment of $Mo(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)$ with a stoichiometric amount of TCNE results in the formation of $[Mo(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)][TCNE]$.[41b] The

Scheme 84

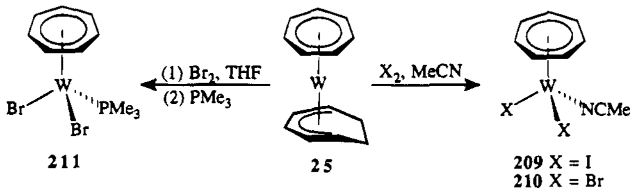


IR, EPR, and magnetic susceptibility measurements reveal that the solid state structure of the salt consists of the diamagnetic dimeric dianion $[TCNE]_2^{2-}$. Similar reaction of Mo(η^7-C_7H_7)(η^5-C_5H_5) and TCNQ gives the 2:1 charge-transfer salt [Mo(η^7-C_7H_7)(η^5-C_5H_5)]$_2$[TCNQ]. Intercalation of M(η^7-C_7H_7)(η^5-C_5H_4-Me) (M = Mo or W) into layered ZrS_2 leads to the intercalates $\{ZrS_2[M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)]_x\}$ [$x = 0.22$ (Mo) or 0.20 (W)] of which the lattice expansion has been determined by X-ray powder diffraction.[42b]

Compound Mo(η^7-C_7H_7)(η^5-C_7H_9) (**5**) undergoes a reversible one-electron oxidation at $E_{1/2} = -0.19$ V relative to the ferrocenium–ferrocene couple (or +0.17 vs SCE) as shown by cyclic voltammetry.[21] Chemical oxidation of **5** to the monocation [Mo(η^7-C_7H_7)(η^5-C_7H_9)]$^+$ (**7**) can be achieved by the action of 1 equiv of $AgBF_4$, excess amount of HBF_4 or 0.5 equiv of I_2. Reduction of **7** back to the corresponding neutral molecule can be effected with 1% sodium amalgam.[21,41] Treatment of **5** with 1 equiv of iodine in THF, however, gives a mixture of **205** and **206**. The air-stable, but thermally-unstable, compound **205** has been crystallographically characterized,[169] while the structure of **206** has only been tentatively assigned on the basis of its spectroscopic data. Both of these compounds react with MeCN and PMe_3 giving **197** and **198**, respectively. An improved route to **197** is the oxidation of **5** with iodine in MeCN from which the air- and thermally-stable **197** can be isolated in 71% yield. Similarly, oxidation of **5** with Br_2 or $PhICl_2$ in THF or toluene, followed by the addition of MeCN results in the formation of **207** or **208**, respectively (Scheme 84).[41,170]

These synthetic routes can be extended to tungsten.[42,170] Thus, treatment of W(η^7-C_7H_7)(η^5-C_7H_9) (**25**) with 1 equiv of I_2 in MeCN gives **209** in excellent yield. By using Br_2 as oxidant, only a small amount of **210** is obtained. However, reaction of **25** with 1 equiv of Br_2 in THF followed by the treatment of PMe_3 leads to the isolation of **211** in moderate yield (Scheme 85).

Scheme 85



It is worth mentioning that the 17-electron complexes M(η^7-C_7H_7)LX_2 (M = Mo or W; L = MeCN or PMe_3; X = Br or I) exhibit antiferromagnetic interactions with temperatures at χ_{max} ranging from 12 to 17 K. The magnetic susceptibility data can be described by one-dimensional magnetic models and this is supported by the crystal structure of Mo(η^7-C_7H_7)(MeCN)I_2 (**197**) which, as shown in Figure 11, reveals the structure to consist of chains of molecules. The shortest intermolecular distance within a chain is 3.670 Å and occurs between I(1) and C(5) of the C_7 ring. This distance is shorter than the sum of the van der Waals radii of carbon and iodine (4.00 Å). The neighboring chains are arranged antiparallel to each other as shown in Figure 11, parts a and d. The distance between the centroids of C_7 rings of adjacent molecules is 3.710 Å, which is close to the interlayer distance of graphite (3.35 Å). Figure 12 shows the temperature variation of magnetic susceptibility for **197**. The maximum at 16 K and the negative Weiss constant (−5.2 K) derived at higher temperature (50−300 K) provide strong evidence for antiferromagnetic interactions. The solid line, which is the theoretical curve based on an one-dimensional Heisenberg model, closely corresponds to the experimental data and from which the values of g (1.84) and exchange constant J (−8.9 K) can be calculated. By similar analyses, the J values for other compounds can also be obtained. Interestingly, some general trends can be observed from these data. Firstly, changing the metal center from Mo to W increases the exchange constant by 1.2−1.9 K, which may be attributed to the fact that the d electrons in W are more diffuse than those in Mo, thus the interaction along the chain between W−W would be stronger than for Mo−Mo. Secondly, changing the ligand from MeCN to PMe_3 decreases the J value by 2.0−3.7 K. It is likely that the more bulky PMe_3 ligand would lengthen the metal−metal separation in the chain resulting in smaller values for J. Finally, changing the halogen from iodine to bromine also decreases the value of J by 0.4−0.7 K. It is noteworthy that the chloro analog Mo(η^7-C_7H_7)(MeCN)Cl_2 (**208**) does not show antiferromagnetic coupling. These may suggest that the efficiency of super-exchange pathway via M−X−M follows the order X = I > Br > Cl.

Reduction of **197** with 1 equiv of Na/Hg in the presence of 2 equiv of PMe_3 or 1 equiv of dmpe or dppe results in the formation of diamagnetic Mo(η^7-C_7H_7)(L)I [L = $(PMe_3)_2$ (**212**), dmpe (**213**), or dppe (**214**)] (Scheme 86).[41] Similarly, treatment of the tungsten complex W(η^7-C_7H_7)(MeCN)I_2 (**209**) with Na/Hg in the presence of dmpe gives W(η^7-C_7H_7)(dmpe)I.[42] The compounds **197**, **209**, and **211** also

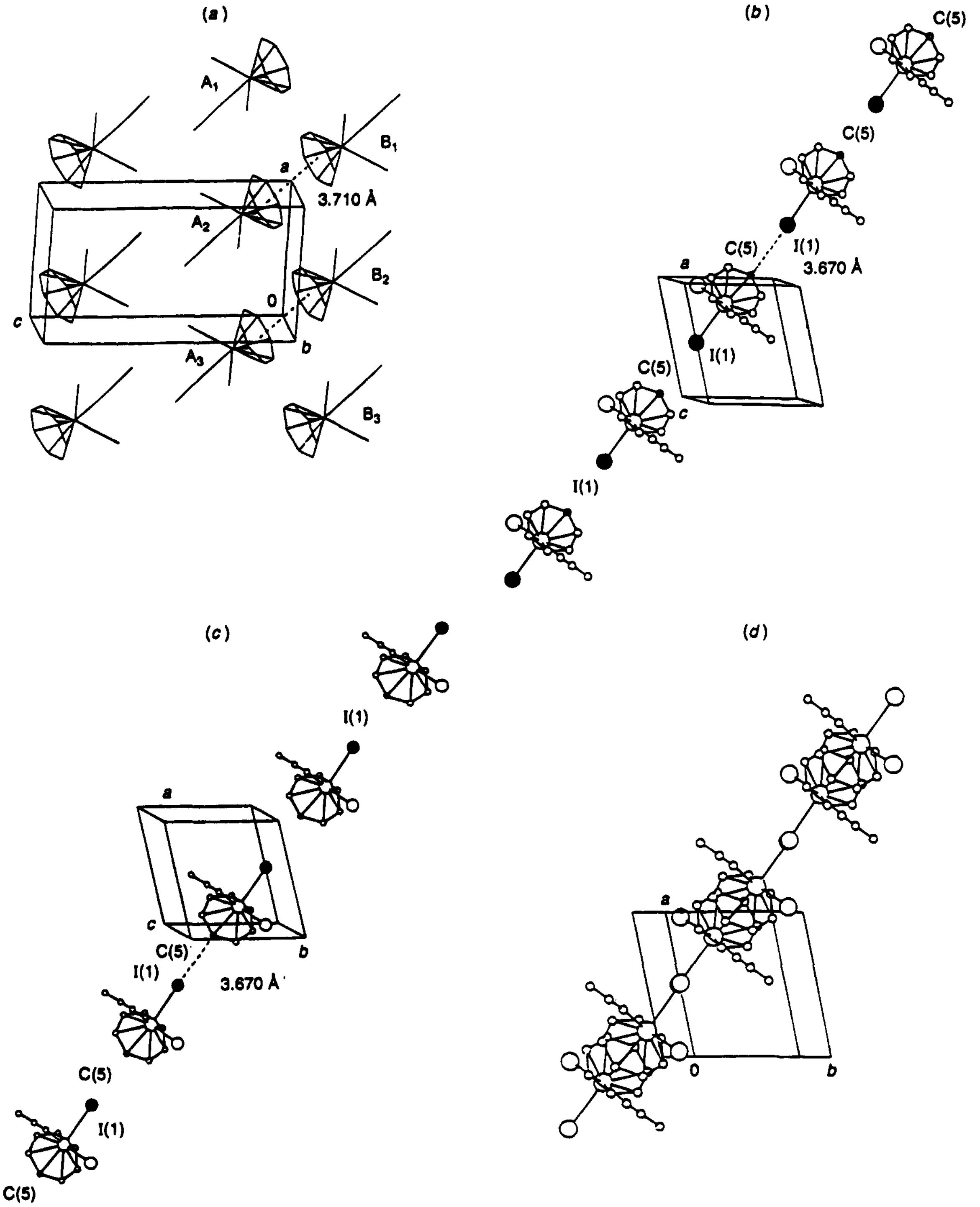


Figure 11. Crystal structure of $Mo(\eta^7-C_7H_7)(MeCN)I_2$: (a) view along the *b* axis, (b) view of molecules A_x along the *c* axis, (c) view of molecules B_x along the *c* axis, (d) view along the *c* axis.

react with an excess of NaC_5H_5, NaC_5H_4Me, or LiC_9H_7 giving the corresponding mixed-sandwich compounds (Scheme 87).[41,42]

The electrochemical reduction of tropylium cation, $[M(\eta^7-C_7H_7)(CO)_3]^+$ [M = Cr (**97**), Mo (**98**), or W (**94**)], and $[Cr(\eta^7-C_7H_6R)(CO)_3]^+$ (R = Me, Et, Pr^i, or Bu^t) has been investigated.[171,172] The free cation undergoes a one-electron reduction leading to the neutral radical $[C_7H_7]^•$, which immediately dimerizes. In contrast, the complexed cations are reduced through a 2-electron reversible step to the corresponding anions $[M(C_7H_6R)(CO)_3]^-$, which, in the absence of proton source, couple with the parent cations, producing the dimer $[M(CO)_3]_2(\eta^6:\eta'^6-C_{14}H_{12}R_2)$. The rate of dimerization is strongly affected by the size of the alkyl group. In MeCN and acetic acid mixture, the anions undergo a competitive attack from protons and cations, and the ratio of the resulting products depends on both the alkyl substituent and the nature of metal. Chemical reduction of **97** and **98** to form the dimer can be achieved with chromium(II) prepared in situ from $CrCl_3·6H_2O$ and zinc.[173] Reaction of **97**, **98**, and **94** with carbonylmetalates $[W(\eta^5-C_5H_5)(CO)_3]^-$ or $[Mn(CO)_5]^-$ does not lead to nucleophilic attack on the C_7 ring. Instead, it gives the corresponding dimers $[M(CO)_3]_2(\eta^6:\eta'^6-C_{14}H_{14})$ in mod-

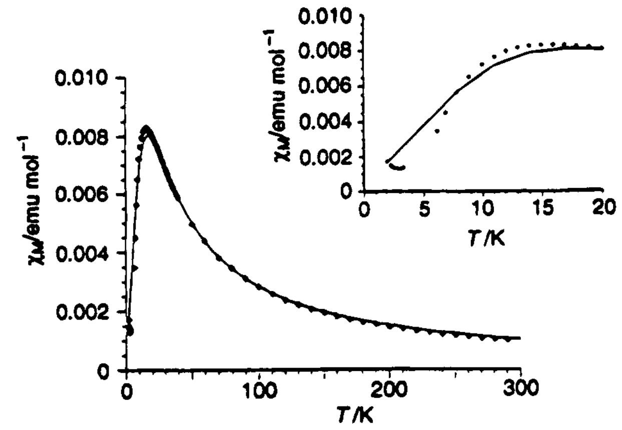
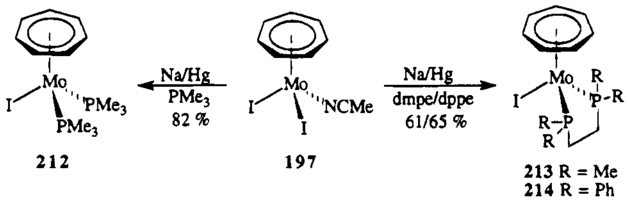
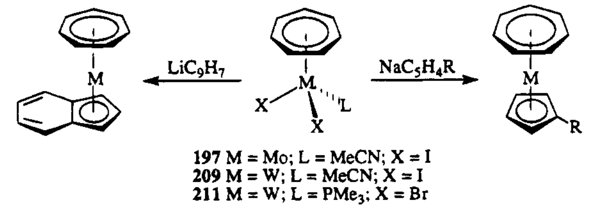


Figure 12. Magnetic susceptibility data for Mo(η^7-C_7H_7)(MeCN)I_2 at 1 T. The solid line is the best fit based on the one-dimensional Heisenberg model. The inset shows an expansion of the low-temperature region.

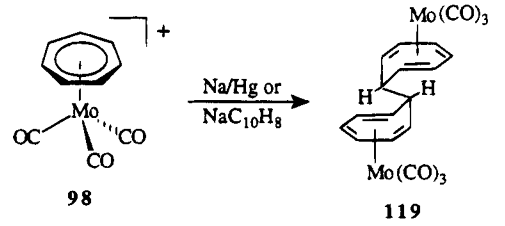
Scheme 86



Scheme 87



Scheme 88



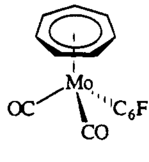
erate yield.[174] Treatment of **98** with either sodium amalgam or sodium naphthalide also leads to reductive dimerization to the ditropyl complex **119**. The X-ray structure of the product confirms that the hydrogen atoms attached to the bridging carbon atoms are both *endo* as shown in Scheme 88.[175]

Recently, the redox behavior of Mo(η^7-C_7H_7)(CO)$_2$(σ-C_6F_5) (**215**) has been examined. It displays a reversible 1 electron oxidation at +0.49 V vs Fc^+/Fc. Chemical oxidation in methanol, however, leads to partial CO insertion giving *ca.* 50% yield of $C_6F_5CO_2Me$ and C_6F_5H.[176] The compound **215** can be reduced either chemically or electrochemically by one electron (E_{pc} = −2.07 V vs Fc^+/Fc) forming the bicycloheptatrienyl dianion **216**.[177] In the presence of $P(OMe)_3$, no significant effect on the electrochemistry of **215** has been observed, but precipitation with hexane gives **217**, of which the structure has been determined.[178] The sodium salt of **216** produced by sodium amalgam reduction is extremely air sensitive and cannot be isolated. However, addition of $[N(PPh_3)_2]^+$ leads to an isolable salt which exists in solution as a mixture of *endo*−*endo*-, *endo*−*exo*-, and *exo*−*exo*-isomers, in which the *endo*−*endo*-isomer has been crystallographically characterized. Reoxidation of **216** rapidly cleaves the bridging C−C bond and regenerates **215**.[177]

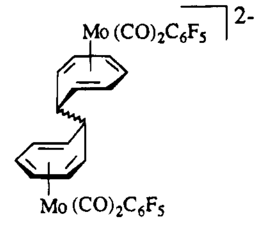
Table 2. Electrochemical Data of Half-Sandwich Cycloheptatrienyl Molybdenum and Tungsten Compounds[135,158b]

compound	$E_{1/2}(0/+1)$ (V)[a]
Mo(η^7-C_7H_7)[P(OMe)$_3$]$_2$I	0.10
Mo(η^7-C_7H_7)[P(OMe)$_3$]$_2$Cl	0.00
Mo(η^7-C_7H_7)(PPh$_3$)(CO)I	0.58
W(η^7-C_7H_7)(PPh$_3$)(CO)I	0.49
[Mo(η^7-C_7H_7)(dppe)(MeCN)]$^+$	0.37[b]
[W(η^7-C_7H_7)(dppe)(MeCN)]$^+$	0.23[b]
Mo(η^7-C_7H_7)(dppe)Cl	−0.05
W(η^7-C_7H_7)(dppe)Cl	−0.21
Mo(η^7-C_7H_7)(dppe)(C≡CPh)	−0.15
Mo(η^7-C_7H_7)(dppe)(C≡CBu^t)	−0.28

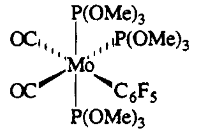
[a] $E_{1/2}$ vs SCE measured in CH_2Cl_2 unless stated otherwise. [b] In MeCN.



215



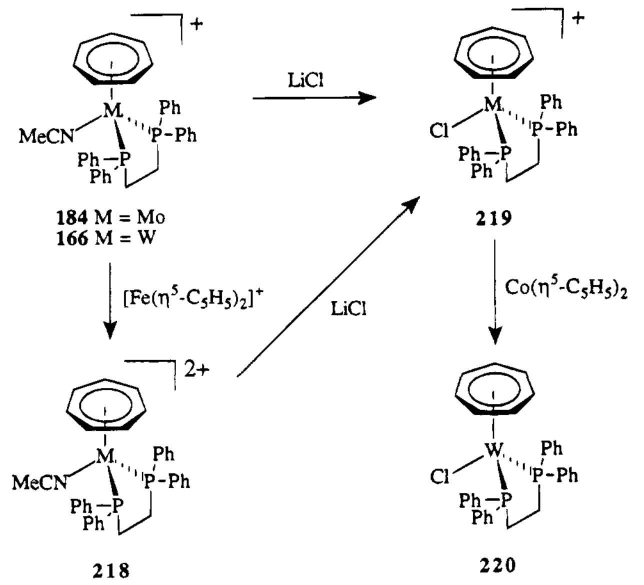
216



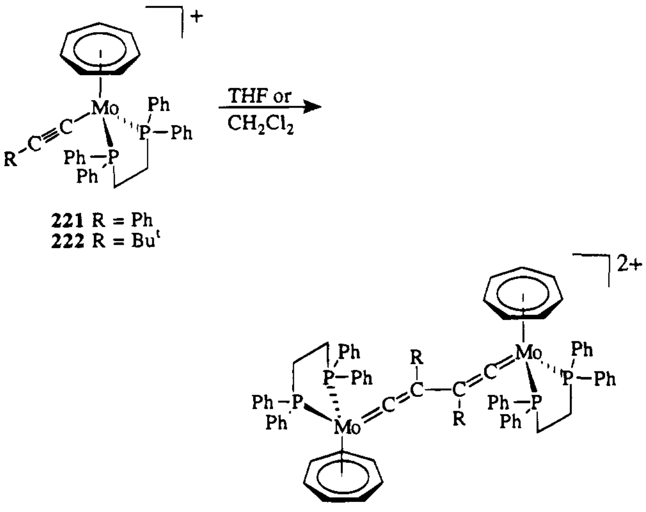
217

Whiteley *et al.* have investigated the electrochemistry of some half-sandwich cycloheptatrienyl derivatives of molybdenum and tungsten.[135,158b] Table 2 lists the $E_{1/2}$ values determined by cyclic voltammetry. All of these complexes undergo a 1-electron transfer process and some of these redox processes can be performed chemically. For example, compound Mo(η^7-C_7H_7)[P(OMe)$_3$]$_2$I (**191**) can be oxidized with [Fe(η^5-C_5H_5)$_2$]$^+$ or [NO]$^+$ to give the corresponding cation, while reduction of {Mo(η^7-C_7H_7)[P(OMe)$_3$]$_2$Cl}$^+$ (**192**) with Co(η^5-C_5H_5)$_2$ affords the corresponding neutral compound.[135] Ferrocenium cation can also be used as oxidant to convert [M(η^7-C_7H_7)(dppe)(MeCN)]$^+$ [M = Mo (**184**) or W (**166**)] to the corresponding dications (**218**). Both of the cations **184** and **166** react with LiCl in acetone forming the paramagnetic species [M(η^7-C_7H_7)(dppe)Cl]$^+$ (**219**). For the reaction with **166**, it requires prolonged reflux in acetone and gives W(η^7-C_7H_7)(dppe)Cl (**220**) as side product. Treatment of the dications **218** with LiCl also gives **219**, but their formation is much faster than that from the corresponding cations. Chemical reduction of **219** (M = W) to **220** with Co(η^5-C_5H_5)$_2$ has also been reported (Scheme 89).[135]

Scheme 89



Scheme 90



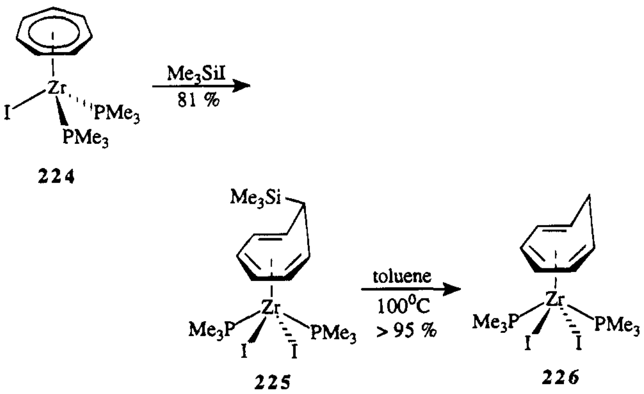
223

Both **187** and **188** can be oxidized with $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ to produce the corresponding cations $[Mo(\eta^7\text{-}C_7H_7)(dppe)(C{\equiv}CR)]^+$ [R = Ph (**221**) or Bu^t (**222**)].[158b] X-ray diffraction studies have been performed on **187** and its monocation **221** which show that the mean Mo—P distance increases and the Mo—C(alkynyl) distance decreases significantly resulting from oxidation. The mean Mo—C(ring) distance and C≡C bond length are virtually unchanged. These observations suggest that the alkynyl ligand in these complexes acts predominantly as a σ-donor to molybdenum with insignificant contribution of $d\pi$ (metal) $\rightarrow$ π^* (alkynyl) interaction to the metal—alkynyl bond.[179] Interestingly, cations **221** and **222** undergo coupling at C_β of the alkynyl ligand to form the divinylidene-bridged, dimer products **223** of which the structure for R = Ph has been confirmed by X-ray studies (Scheme 90).[180]

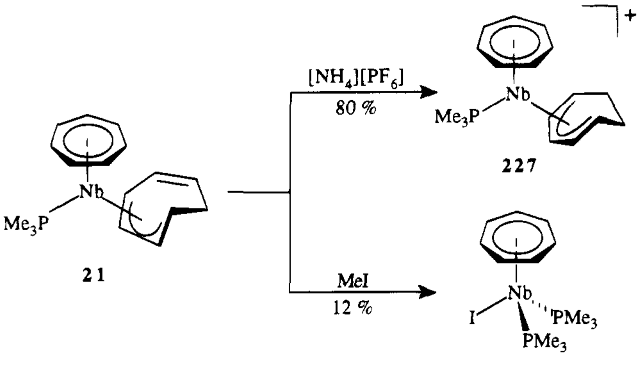
6. Other Reactions

The catalytic properties of cycloheptatrienylmetal complexes have been briefly examined. The dimer $[Ti(\eta^7\text{-}C_7H_7)(THF)(\mu\text{-}Cl)]_2$ (**11**) in conjunction with $(AlEt_2Cl)_2$ catalyzes ethylene polymerization. The activity of the catalyst system is highly variable as a function of varying proportions. The best activity number for the catalyst achieved is 0.11 g of polyethylene per hour per atmosphere of ethylene per millimole of catalyst.[22b] Recently, it has been found that the 17-electron complex $Mo(\eta^7\text{-}C_7H_7)(MeCN)I_2$ (**197**), activated with Me_3SiCH_2MgCl, is a catalyst for ring-opening metathesis polymerization of norbornene. In a preliminary study, **197**/Me_3SiCH_2MgCl reacts with 300 equiv of norbornene (2 g) in toluene at room temperature for 17 h produces 0.2 g of polynorbornene. Noteworthy, essentially all of the double bonds in the polymer are in the *trans*-configuration as determined by ^{13}C NMR spectroscopy. The tungsten analog $W(\eta^7\text{-}C_7H_7)(MeCN)I_2$ (**209**) behaves in a similar manner, except that the reactivity of this catalyst system is higher (1 g of norbornene gives 0.58 g of polymer under similar conditions) and the selectivity is lower (the resulting polymer has a *trans*:*cis* ratio of 2.2:1).[164]

Scheme 91



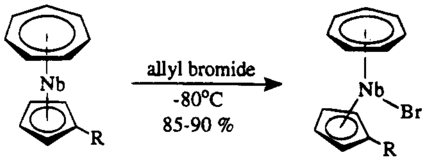
Scheme 92



The reaction of $Zr(\eta^7\text{-}C_7H_7)(PMe_3)_2I$ (**224**) with Me_3SiI unexpectedly produces the crystallographically characterized *exo*-substituted cycloheptatriene complex **225** in high yield. This compound is thermally sensitive, and upon heating in toluene at 100 °C gives **226** (Scheme 91). When perdeuteriotoluene is used as solvent there is no observable incorporation of deuterium into **226**.[26b,27]

Protonation of **21** with $[NH_4][PF_6]$ affords good yields of **227**, whereas reaction of **21** with iodomethane gives the unexpected paramagnetic compound **228** in 12% yield (Scheme 92). The X-ray structure of **228** has been determined. The sandwich compounds **71** and **72** react with 1 equiv of allyl

Scheme 93



71 R = H
72 R = Me

229

bromide at −80 °C yielding the bent mixed-sandwich compounds **229** in excellent yield (Scheme 93).[35]

VII. Concluding Remarks

A rich and diverse chemistry of the cycloheptatriene and -enyl compounds of the early transition metals has been developed in the period covered in this article. The preparations of many useful synthons have been discovered and the nature of the η-cycloheptatrienyl−transition metal bonding has been clarified. There are clearly many possibilities for the future development of the chemistry of η-cycloheptatrienyl complexes. Applications in homogeneous catalysis have been little studied but it seems probable that the unique properties of the η-cycloheptatrienyl ligand will find a role in this area. Also, there remains the challenge to develop areas such as η-cycloheptatrienyl−lanthanide chemistry, for example, neutral compounds in the general class $[M(\eta\text{-}C_7H_7)L_3]$, where L is a 2-electron donor ligand. η-Cycloheptatrienyl transition metal systems in combination with other hydrocarbyl ligands such as carbenes, carbynes, polyhydrides are either unknown or scarcely studied. We hope this article will stimulate further research into C_7-ring chemistry.

VIII. Acknowledgements

We gratefully acknowledge the Croucher Foundation of Hong Kong for financial support to D.K.P.N. during his graduate study.

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