Reviews

Synthesis and Reactivity of Heteropentadienyl−Transition-Metal Complexes

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The synthesis and reactivity of transition-metal complexes containing heteropentadienyl ligands (i.e., pentadienyl analogues in which one terminal carbon has been replaced by a heteroatom) are reviewed. Specifically, four compound classes are covered: oxapentadienyl−metal, azapentadienyl−metal, thiapentadienyl−metal, and phosphapentadienyl−metal complexes. Within each of these classes, contributions are presented in approximate chronological order. Particular attention is given to the development of rational synthetic methodologies. A second focus is the unique reactivity of these compounds, much of which stems from the ability of the heteropentadienyl ligands to adopt a variety of bonding modes and shuttle easily between them.

I. Introduction

During the past 25 years, transition-metal complexes containing the acyclic pentadienyl ligand have been extensively investigated, and several excellent reviews of this subject have appeared.[1] By comparison, substantially less effort has been directed toward synthesizing and studying the chemistry of heteropentadienyl−metal complexes: i.e., species in which one carbon of the pentadienyl ligand has been replaced with a heteroatom. However, general synthetic methods are now available (particularly for the oxa and thia systems), and the rich reaction chemistry of these compounds is under active investigation.

One of the key features of heteropentadienyl ligands is their ability to adopt a variety of bonding modes and to shuttle easily between them. This, in turn, leads to enhanced reactivity at the metal center and raises the intriguing possibility of using heteropentadienyl ligand shifts ($\eta^5 \rightleftarrows \eta^3 \rightleftarrows \eta^1$) to open and close coordination sites in a catalytic cycle. While such a cycle has not yet been achieved, many of the essential steps have been demonstrated.

This review focuses on four classes of heteropentadienyl−metal complexes: oxapentadienyl−metal, azapentadienyl−metal, thiapentadienyl−metal, and phosphapentadienyl−metal. Only heteropentadienyl ligands in which the heteroatom (O, N, S, or P) resides in a *terminal* position on the chain are considered. For purposes of nomenclature, the heteroatom is numbered as atom 5 in the chain; hence, the terminal carbon is C1 and the carbon adjacent to the heteroatom is C4.

Within each class of heteropentadienyl−metal complexes, contributions are generally presented in chronological order, but closely related pieces of work are discussed together. The focus of the review is on synthesis and reactivity rather than structure and spectroscopy. While some key X-ray structural data are presented, most are left for the reader to explore independently.

The reactivity of heteropentadienyl−metal complexes is a significant topic in this review, but the focus is on *organometallic* reactivity rather than on organic reactions of the heteropentadienyl ligand. Hence, reactions that occur at the metal center such as ligand addition and oxidative addition are reviewed. Also included are reactions involving simple electrophiles such as H^+ and Me^+. Although these reactions may occur directly on the heteropentadienyl ligand, they often lead to a change in the heteropentadienyl ligand's interaction with the metal center. Generally *not* included are organic reactions that involve *only* the heteropentadienyl ligand and do not lead to a shift in the heteropentadienyl bonding mode.

It should be noted that many different names have been used over the years for heteropentadienyl ligands. For example, η^3-oxapentadienyl ligands are often referred to in the literature as allyl aldehydes or allyl ketones, while thiapentadienyls are often called butadienethiolate ligands. My apologies to those readers who prefer the alternative names!

II. Oxapentadienyl−Metal Complexes

A. Early Work. The first example of an oxapentadienyl−metal complex, [((1,2,3-η)-2,4-dimethyl-5-oxapentadienyl)Pd(Cl)]$_2$ (**1**), was synthesized in 1959 by Moiseev[2] and fully characterized by NMR and IR spectroscopy in 1962 by Parshall and Wilkinson.[3] As shown in Scheme 1, this dimeric species was prepared by simply

(1) (a) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255. (b) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15. (c) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125. (d) Ernst, R. D. *Comments Inorg. Chem.* **1999**, *21*, 285.

(2) Moiseev, I. I.; Feodorovskaya, E. A.; Syrkin, Ya. K. *Russ. J. Inorg. Chem.* **1959**, *4*, 1218.

(3) (a) Parshall, G. W.; Wilkinson, G. *Chem. Ind. (London)* **1962**, 261. (b) Parshall, G. W.; Wilkinson, G. *Inorg. Chem.* **1962**, *1*, 896.

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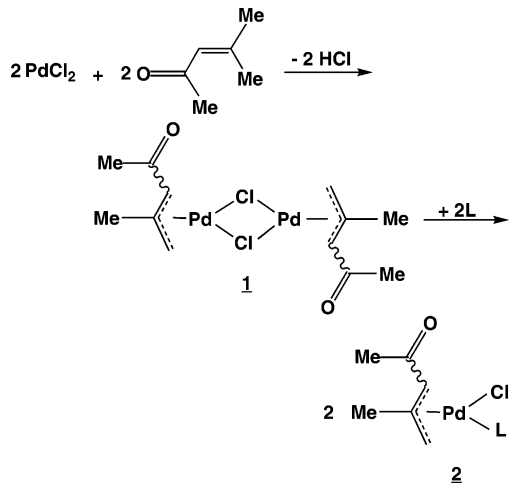
Scheme 1



reacting Pd(II) chloride or sodium chloropalladite with mesityl oxide. Treatment of **1** with 2e donor ligands, L, including PPh_3 and 2-methylpyridine, led to the breakup of the dimer and production of the monomeric species **2**. The NMR data for these monomers suggested the presence of noninterconverting *syn*-η^3 and *anti*-η^3 isomers in solution.

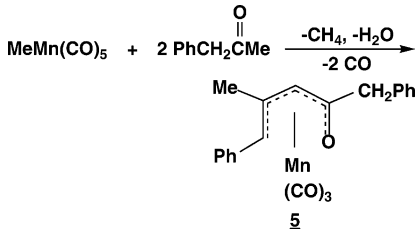
In 1964, Tsuji et al.[4] reported that α,β- or β,γ-unsaturated carboxylic esters also reacted with Pd(II) chloride (or other Pd(II) salts) to generate dimeric products analogous to **1** but containing ester groups (COOR) in place of the acetyls.

During the 25 years following Tsuji's 1964 paper, there was a smattering of serendipitous syntheses of oxapentadienyl−metal complexes. The first of these was reported in 1966 by Bannister and Green,[5] who found that $RMn(CO)_5$ (R = Me, Ph) reacted with butadiene to produce the η^3-oxapentadienyl−Mn complexes **3a**,**b** (Scheme 2), perhaps through the intermediacy of species **A**−**C**. Upon heating, the phenyl derivative (**3b**) reversibly lost CO to produce the first example of an η^5-oxapentadienyl−metal complex, **4b**.

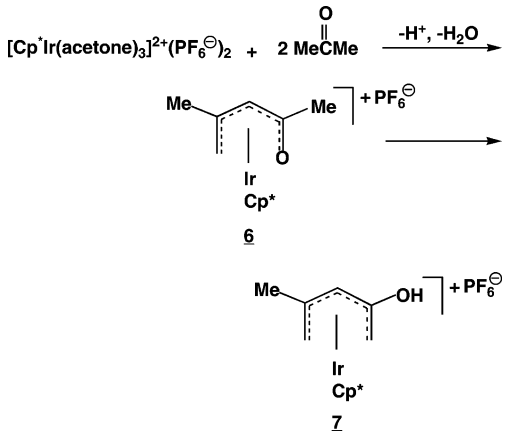
In 1975, Bennett and Bruce[6] isolated a related η^5-oxapentadienyl−Mn complex (**5**; Scheme 3) from the reaction of $MeMn(CO)_5$ with benzyl methyl ketone. In this reaction, the oxapentadienyl ligand was apparently formed through a transition-metal-induced aldol condensation of two benzyl methyl ketone molecules. The methyl group originally present on the manganese reagent was eliminated as methane.

In a similar vein, Maitlis[7] found that $[Cp^*Ir(acetone)_3]^{2+}(PF_6^-)_2$ led to the formation of [(η^5-2-methyl-4-hydroxypentadienyl)Ir-(Cp*)]$^+PF_6^-$ (**7**; Scheme 4). He postulated the intermediacy of an η^5-oxapentadienyl−Ir complex, **6**, in which the 2,4-dimethyl-5-oxapentadienyl ligand was formed through the aldol condensation of two acetone molecules. Later, Maitlis succeeded in synthesizing **6** directly from $[Cp^*Ir(acetone)_3]^{2+}(PF_6^-)_2$ and mesityl oxide.

Scheme 3

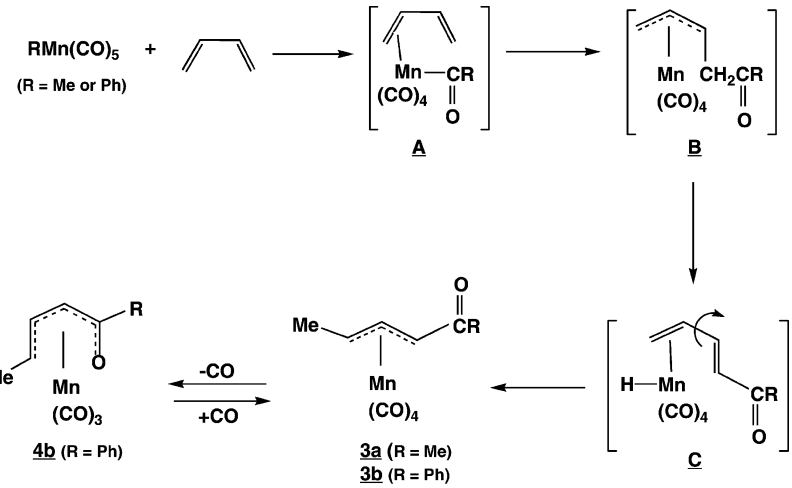


Scheme 4

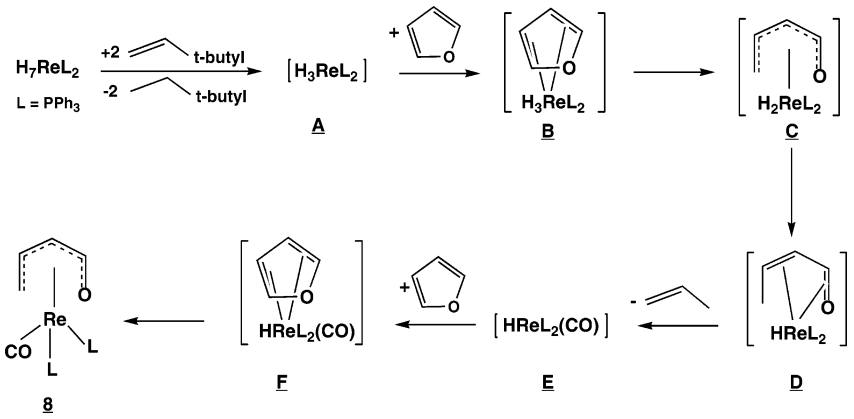


In 1983, Felkin[8] discovered that treatment of $H_7Re(PPh_3)_2$ with furan in the presence of a hydrogen acceptor olefin, *tert*-butylethylene, led to furan ring opening and production of (η^5-oxapentadienyl)$Re(PPh_3)_2$(CO) (**8**; Scheme 5). In this complex reaction, a mechanism for which is postulated in Scheme 5, two furan

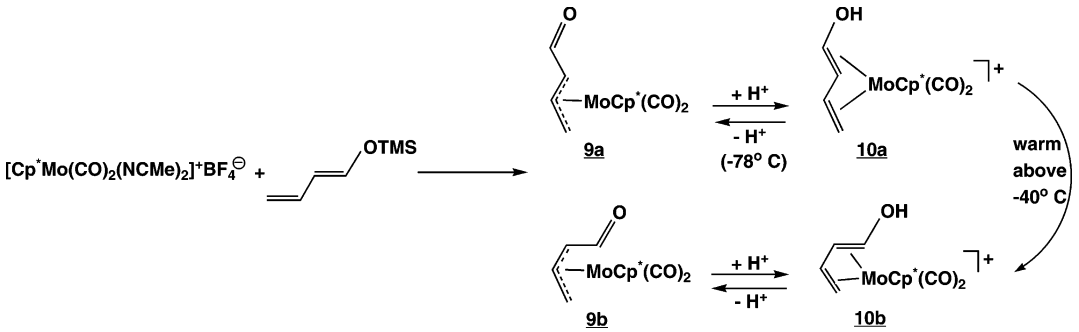
Scheme 2



Scheme 5



Scheme 6



rings were opened; one was converted into propene and the carbonyl ligand, while the other became the oxapentadienyl ligand. Compound **8** was the first unsubstituted oxapentadienyl−metal complex and the first to be characterized by X-ray diffraction. In the X-ray crystal structure, the oxapentadienyl ligand was planar and the C−C bond lengths were all equal (1.40 Å), indicating a fully delocalized six-π-electron, η^5-donor.

B. Oxapentadienyl−Metal Complexes from ((Trimethylsilyl)oxy)butadiene−Metal Precursors. In 1989, two new *rational* approaches to the synthesis of oxapentadienyl−metal complexes were introduced independently by Green and by Liu. First, Green[9] showed that the reaction of $[Cp^*Mo(CO)_2(NCMe)_2]^+BF_4^-$ with 1-((trimethylsilyl)oxy)buta-1,3-diene led to the production of ((1,2,3-η)-5-oxapentadienyl)Mo(Cp*)(CO)$_2$ (**9a,b**; Scheme 6) via coordination of the 1,3-diene, followed by rapid fluoride anion initiated desilylation. While the *syn*-η^3-oxapentadienyl isomer (**9a**) dominated, a small amount of the *anti*-η^3 isomer (**9b**) was also observed, and the two isomers could be separated by chromatography. Low-temperature (−78 °C) protonation of **9a**,**b** led to H^+ attack on oxygen, producing the η^4-*s-trans*- and η^4-*s-cis*-1-hydroxy-1,3-butadiene complexes **10a**,**b**, respectively (see Scheme 6). When it was warmed above −40 °C, the η^4-*s-trans* ligand irreversibly isomerized to the more stable η^4-*s-cis* form, and subsequent deprotonation of **10b** with NEt_3 generated the *anti*-η^3-oxapentadienyl complex, **9b**, cleanly.

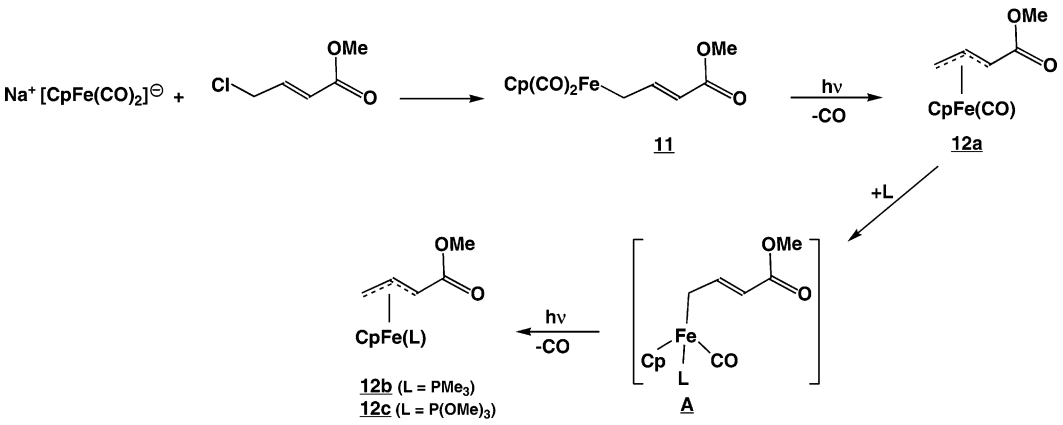
Green[10] later demonstrated that this same synthetic approach could be used to produce oxapentadienyl−*ruthenium* complexes. In particular, the reaction of $[CpRu(CO)(NCMe)_2]^+ BF_4^-$ with 1-((trimethylsilyl)oxy)-buta-1,3-diene cleanly generated (η^3-oxapentadienyl)-Ru(Cp)(CO) as the *syn* isomer. As above, protonation at oxygen produced the η^4-*s-trans*-1-hydroxy-1,3-butadiene product, which rearranged ($t_{1/2}$ = 2 h at 25 °C) to the η^4-*s-cis* isomer. Deprotonation with NEt_3 cleanly generated the *anti*-η^3-oxapentadienyl complex.

C. Oxapentadienyl−Metal Complexes from Anionic Metal Complexes and Halogenated Esters or Ketones. Also in 1989, Liu[11] introduced a second rational approach to oxapentadienyl−metal complexes. Liu's method involved the use of anionic metal complexes and γ-chlorinated α,β-unsaturated esters, an approach that had earlier proved successful in the synthesis of pentadienyl−metal complexes. In a typical reaction, $Na^+[CpFe(CO)_2]^-$ was reacted with methyl 4-chloro-2-butenoate, producing (1-η-4-methoxy-5-oxapentadienyl)Fe(Cp)(CO)$_2$ (**11**; Scheme 7) via an S_N2 reaction.

Compound **11** readily lost CO under photolysis to produce the η^3-oxapentadienyl−Fe complex **12a**. Interestingly, further photolysis or heating of **12a** did *not* lead to the "half-open" ferrocene, (η^5-4-methoxy-5-oxapentadienyl)Fe(Cp). However, irradiation of **12a** in the presence of phosphines or phosphites led to carbonyl replacement and synthesis of ((1,2,3-η)-4-methoxy-5-oxapentadienyl)Fe(Cp)(L) (**12b**, L = PMe_3; **12c**, L =

(4) Tsuji, J.; Imamura, S.; Kiji, J. *J. Am. Chem. Soc.* **1964**, *86*, 4491.
(5) (a) Bannister, W. D.; Green, M.; Haszeldine, R. N. *J. Chem. Soc. A* **1966**, 194. (b) Green, M.; Hancock, R. I. *J. Chem. Soc. A* **1968**, 109.
(6) Bennett, R. L.; Bruce, M. I. *Aust. J. Chem.* **1975**, *28*, 1141.
(7) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *134*, 319.
(8) Baudry, D.; Daran, J.-C.; Dromzee, Y.; Ephritikhine, M.; Felkin, H.; Jeannin, Y.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1983**, 813.
(9) (a) Benyunes, S. A.; Green, M.; Grimshire, M. J. *Organometallics* **1989**, *8*, 2268. (b) Benyunes, S. A.; Binelli, A.; Green, M.; Grimshire, M. J. *J. Chem. Soc., Dalton Trans.* **1991**, 895.

Scheme 7



Scheme 8

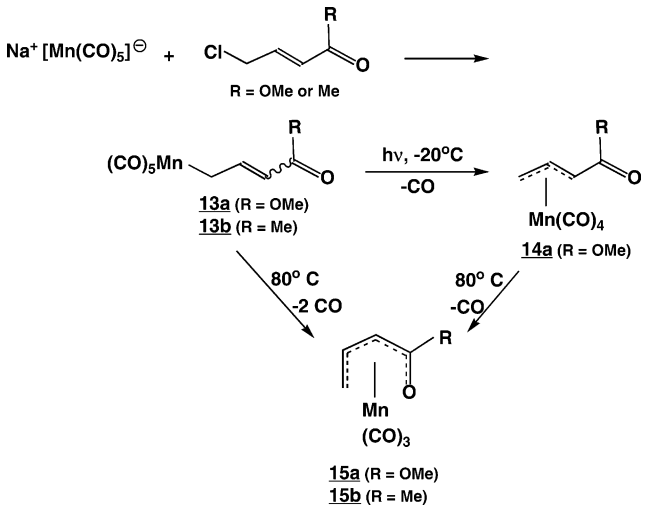
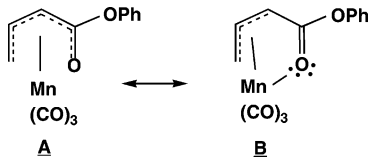


Chart 1



P(OMe)$_3$), probably via the η^1-oxapentadienyl−Fe intermediate **A** (Scheme 7).

Liu was able to demonstrate the generality of this synthetic methodology by applying it to the analogous manganese[12] and molybdenum[13] systems. In the manganese system, for example, treatment of Na$^+$[Mn(CO)$_5$]$^-$ with methyl 4-chloro-2-butenoate or 5-chloro-3-penten-2-one produced the η^1-oxapentadienyl−Mn complexes **13a**,**b** (Scheme 8). Low-temperature photolysis of **13a** led to CO loss and production of the *syn*-η^3-oxapentadienyl complex **14a**. Heating of **13a** or **14a** in cyclohexane at reflux resulted in the production of the η^5-oxapentadienyl complex **15a**. Compound **13b** was likewise converted to **15b** upon heating.

The rotational barrier of the η^5-oxapentadienyl ligand with respect to the Mn(CO)$_3$ moiety in **15a**,**b** was measured by variable-temperature ^{13}C NMR spectroscopy and found to be 15.6−15.8 kcal/mol. This barrier is somewhat higher than that commonly observed for analogous η^5-*pentadienyl*−metal complexes containing small ligands (10−14 kcal/mol).[1a]

One interesting feature of the chemistry of **15a**,**b** was the facile nature of the $\eta^5 \rightleftarrows \eta^3$ oxapentadienyl ligand rearrangement. Hence, treatment of **15a**,**b** with phosphine ligands (L) led to the production of ((1,2,3-η)-4-R-5-oxapentadienyl)Mn(CO)$_3$(L) (L = PMe$_3$, PPh$_3$), which, upon heating in cyclohexane at reflux, lost CO to produce (η^5-4-R-5-oxapentadienyl)Mn(CO)$_2$(L). **15a** even reacted with weakly coordinating solvent molecules, S, including acetonitrile, acetone, and THF, to produce ((1,2,3-η)-4-R-5-oxapentadienyl)Mn(CO)$_3$(S) complexes. These $\eta^5 \rightarrow \eta^3$ "slippage" reactions are apparently promoted by a relatively weak interaction between the carbon−oxygen π-bond and the metal center.

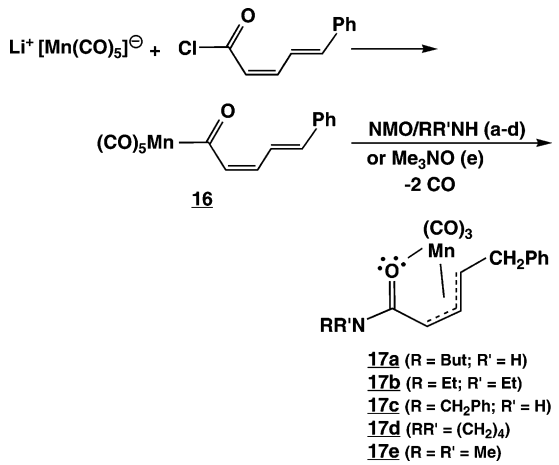
Sorensen[14] independently reported virtually the same oxapentadienyl−Mn chemistry as Liu but used ethyl and phenyl 4-chloro-2-butenoate as substrates rather than Liu's methyl ester. The OEt- and OPh-substituted compounds (**13c**,**d**, **14c**,**d**, and **15c**,**d**) were isolated, and all three of the OPh derivatives were characterized by X-ray diffraction.

It is interesting to compare Liu's structure of (η^5-4-methyl-5-oxapentadienyl)Mn(CO)$_3$ (**15b**) with Sorensen's structure of (η^5-4-phenoxy-5-oxapentadienyl)Mn(CO)$_3$ (**15d**). Due to the presence of the OPh substituent in Sorensen's ligand, C4 is displaced up and away from the manganese center, so that the Mn−C4 distance is 2.369(5) Å, vs 2.213(4) Å in Liu's compound. Hence, in Sorensen's derivative there appears to be an important contribution from resonance structure **B** in Chart 1. This is further supported by the longer C3−C4 distance in **15d** vs **15b** (1.441(7) Å vs 1.403(5) Å).

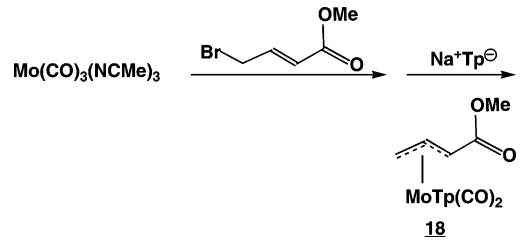
A similar but even more pronounced "η^1,η^3" distortion was observed in a related oxapentadienyl−Mn complex produced by Allison.[15] As shown in Scheme 9, treatment of Li$^+$[Mn(CO)$_5$]$^-$ with 5-phenylpentadienoyl chloride produced the η^1-pentadienoyl complex **16**, which when reacted with *N*-methylmorpholine *N*-oxide (NMO) and selected amines or with Me$_3$NO produced the oxapen-

(10) Benyunes, S. A.; Day, J. P.; Green, M.; Al-Saadoon, A. W.; Waring, T. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1416.
(11) Cheng, M.-H.; Wu, Y.-J.; Wang, S.-L.; Liu, R.-S. *J. Organomet. Chem.* **1989**, *373*, 119.
(12) Cheng, M.-H.; Cheng, C.-Y.; Wang, S.-L.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1990**, *9*, 1853.
(13) Vong, W.-J.; Peng, S.-M.; Lin, S.-H.; Lin, W.-J.; Liu, R.-S. *J. Am. Chem. Soc.* **1991**, *113*, 573.
(14) (a) Masters, A. P.; Sorensen, T. S. *Can. J. Chem.* **1990**, *68*, 492. (b) Masters, A. P.; Richardson, J. F.; Sorensen, T. S. *Can. J. Chem.* **1990**, *68*, 2221.
(15) AbuBaker, A.; Bryan, C. D.; Cordes, A. W.; Allison, N. T. *Organometallics* **1994**, *13*, 3375.

Scheme 9



Scheme 10



tadienyl−Mn complexes **17a**−**e**. The structure of **17e** (R = R′ = Me) revealed a very nonplanar oxapentadienyl ligand, in which the Mn−C4 distance was 2.49(2) Å and the C3−C4 bond length was 1.48(2) Å.

A likely explanation for these "η^1,η^3" distortions in **15d** and **17e** is that electron donation from the OPh or NMe_2 substituent increases the basicity of the oxapentadienyl oxygen center, enhancing its ability to serve as a 2e σ-donor. Concomitantly, the interaction between the C−O π-bond and the metal center is weakened.

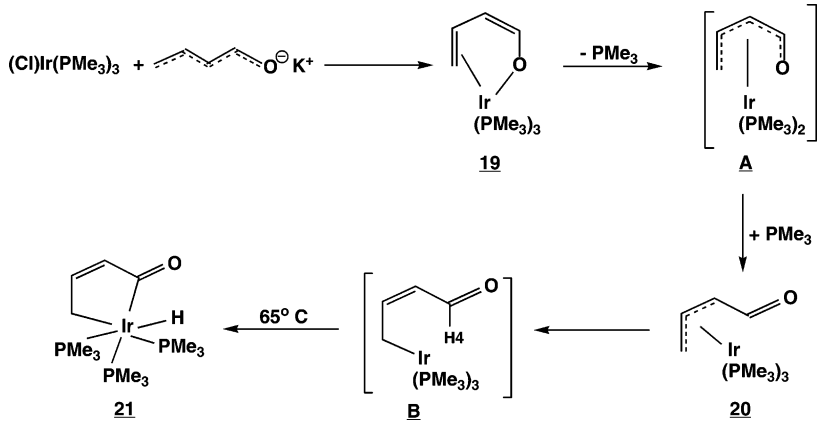
One final synthesis that utilized a halogenated ester substrate but a *neutral* metal reagent was recently developed by Pearson.[16] In the Pearson system, $Mo(CO)_3(NCMe)_3$ was first reacted with methyl 4-bromo-2-butenoate and then with sodium tris(1-pyrazoyl)-borohydride (Na^+Tp^-), producing ((1,2,3-η)-4-methoxy-5-oxapentadienyl)Mo(Tp)$(CO)_2$ (**18**; Scheme 10). The mechanism of this reaction involves initial oxidative addition of the C−Br bond to the molybdenum center, followed by displacement of Br^- by Tp^-.

D. Oxapentadienyl−Metal Complexes from Anionic Oxapentadienide Reagents and Metal Halides. My research group began working in the area of oxapentadienyl−metal chemistry in 1990. Like Liu's group, we were already involved in the study of pentadienyl−metal complexes and were interested in how replacement of a CH_2 moiety with an oxygen atom in the pentadienyl chain would affect the chemistry. Our synthetic strategy was to use anionic oxapentadienide reagents and metal halides, an approach that closely modeled the work we had done earlier with anionic *pentadienide* reagents.

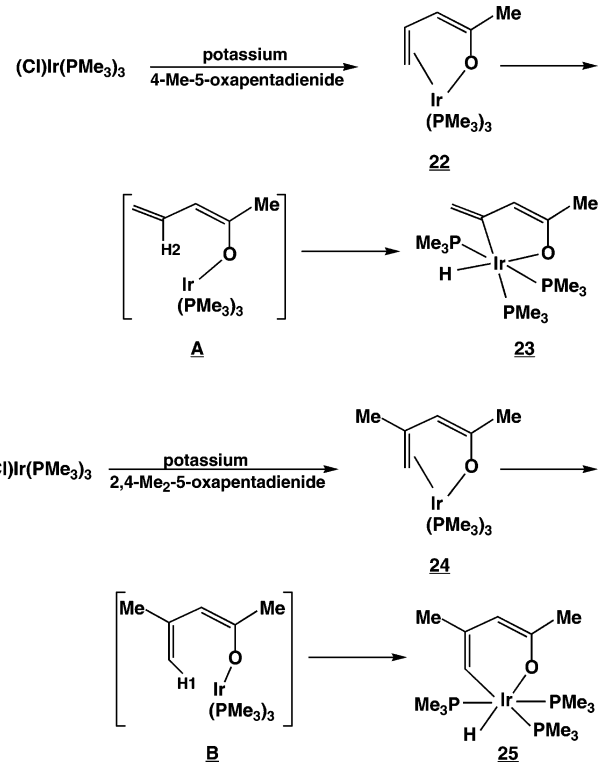
A quick search of the literature revealed that Kloosterziel[17] had previously reported the synthesis of potassium 5-oxapentadienide from the reaction of crotonaldehyde with potassium amide in liquid ammonia. The NMR data indicated that in solution the anion was W-shaped.[17,18] We repeated the Kloosterziel synthesis, isolated potassium oxapentadienide as a yellow powder, and then reacted it with $(Cl)Ir(PMe_3)_3$.[19a,b] As shown in Scheme 11, the initially formed product was ((1,2,5-η)-5-oxapentadienyl)$Ir(PMe_3)_3$ (**19**), which resulted from nucleophilic displacement of the chloride by the oxygen atom of the oxapentadienide reagent, followed by π-coordination of the terminal double bond. Over a period of several hours at room temperature, **19** rearranged to ((1,2,3-η)-5-oxapentadienyl)$Ir(PMe_3)_3$ (**20**), in which the η^3-oxapentadienyl ligand adopted a sickle-shaped *anti* configuration (as shown). This oxapentadienyl ligand rearrangement probably involved the intermediacy of (η^5-oxapentadienyl)$Ir(PMe_3)_2$ (**A**; Scheme 11). Upon heating in THF at reflux, **20** underwent activation of C−H4 to produce an iridacyclopentenone complex (**21**, Scheme 11).

Using the method of Kloosterziel, we were able to synthesize two methylated oxapentadienide reagents, potassium 4-methyl-5-oxapentadienide and potassium 2,4-dimethyl-5-oxapentadienide.[19c] As shown in Scheme 12, each of these oxapentadienide salts was reacted with $(Cl)Ir(PMe_3)_3$ and, in each case, (1,2,5-η)-5-oxapentadienyl products, **22** and **24**, respectively, were observed as the kinetic products. However, both reactions ultimately led to metallacycles formed via C−H bond activation. In the reaction involving 4-methyl-5-oxapentadienide, activation occurred at C−H2 to produce iridaoxacyclopentene **23**, while the reaction involving 2,4-dimethyl-5-oxapentadienide led to C−H1 activation and production of iridaoxacyclohexadiene **25**. Note that,

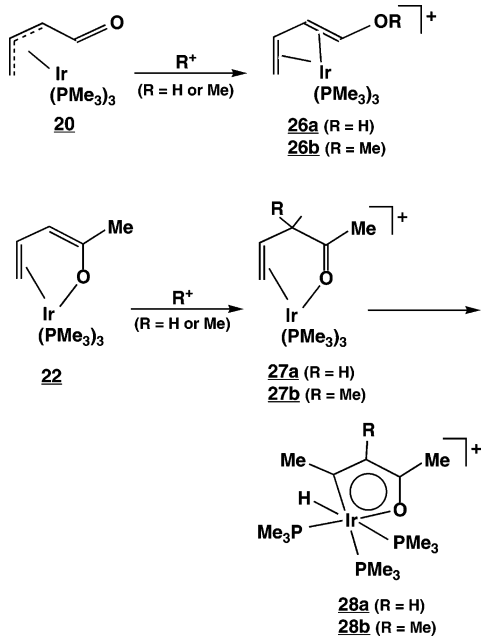
Scheme 11



Scheme 12



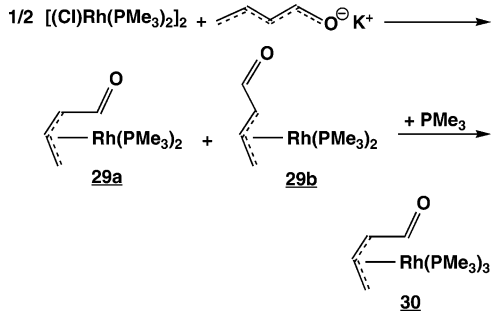
Scheme 13



in each case, methylation at C4 prevented formation of an iridacyclopentenone product such as **21**.

The reactions of ((1,2,3-η)-5-oxapentadienyl)Ir(PMe_3)$_3$ (**20**) and ((1,2,5-η)-4-methyl-5-oxapentadienyl)Ir(PMe_3)$_3$ (**22**) with simple electrophiles were investigated (see Scheme 13). Both H^+ (from HBF_4·OEt_2) and Me^+ (from MeOTf) attacked **20** at the oxygen center, producing the η^4-butadiene products **26**.[19d] In contrast, electrophiles added to **22** at C3, producing the (1,2,5-η)-5-oxapenta-1,4-diene products **27**. These species ultimately rearranged to "metallafurans" (**28**) upon warming.[19e]

Scheme 14



The reactions of (Cl)Ir(PEt_3)$_3$ with the three potassium oxapentadienide reagents were also explored.[19a,b] As in the tris(PMe_3) system, the *final* product of each reaction was a metallacycle, which resulted from activation at C−H4, C−H2, or C−H1. However, in these reactions, the oxapentadienyl−Ir intermediates were not observable by NMR. Apparently, the steric bulk of the PEt_3 ligands destabilized the interaction between iridium and the oxapentadienyl π bonds, allowing oxidative addition to occur from 16e (η^1-oxapentadienyl)-Ir(PEt_3)$_3$ intermediates (cf., Schemes 11 and 12).

More recently, we have expanded our study to include rhodium.[20] Treatment of [(Cl)Rh(PMe_3)$_2$]$_2$ with potassium oxapentadienide produced an equilibrium mixture of 16e *anti*- and *syn*-((1,2,3-η)-5-oxapentadienyl)Rh-(PMe_3)$_2$ (**29a**,**b**; Scheme 14) in an approximate 3:2 ratio. On the basis of the previous iridium chemistry, it is tempting to speculate that these reactions involve an *initial* oxygen-based attack of oxapentadienide on rhodium, followed by rearrangement. While these proposed oxygen-coordinated species are not detected by NMR spectroscopy, the rearrangement from 1,2,5-η to 1,2,3-η may be extremely rapid in this case, because it could proceed through an (η^5-oxapentadienyl)Rh(PMe_3)$_2$ intermediate *without* the prior loss of phosphine (recall the conversion of **19** to **20**; Scheme 11).

Addition of 1 equiv of PMe_3 to **29a**,**b** produced 18e ((1,2,3-η)-5-oxapentadienyl)Rh(PMe_3)$_3$ (**30**; Scheme 14), and only the sickle-shaped *anti* isomer was detected by NMR spectroscopy. Similar results were obtained when 2,4-dimethyl-5-oxapentadienide was used in this reaction system.

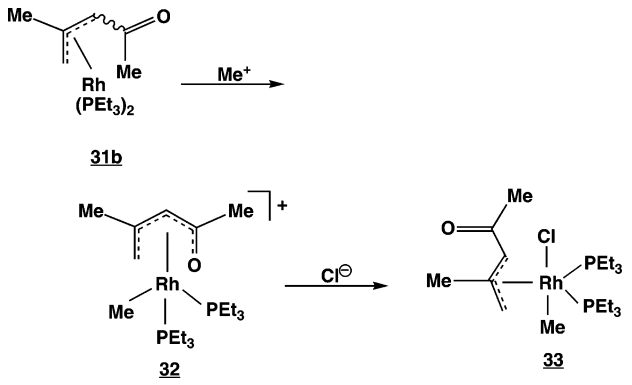
When [(Cl)Rh(PEt_3)$_2$]$_2$ was treated with potassium oxapentadienide or potassium 2,4-dimethyl-5-oxapentadienide, *anti* and *syn* isomers of ((1,2,3-η)-5-oxapentadienyl)Rh(PEt_3)$_2$ (**31a**) or ((1,2,3-η)-2,4-dimethyl-5-oxapentadienyl)Rh(PEt_3)$_2$ (**31b**) were produced, but these complexes were unreactive toward additional PEt_3 at room temperature, apparently for steric reasons. Treatment of **31b** with methyl triflate resulted in methylation at the rhodium center and rearrangement of the η^3-oxapentadienyl ligand to the η^5 bonding mode, producing **32** (Scheme 15). Upon addition of PPN^+Cl^- to **32**, the η^5-oxapentadienyl ligand returned to an η^3 mode and adopted exclusively a syn geometry (**33**; Scheme 15).

(16) Pearson, A. J.; Neagu, I. B.; Pinkerton, A. A.; Kirschbaum, K.; Hardie, M. J. *Organometallics* **1997**, *16*, 4346.

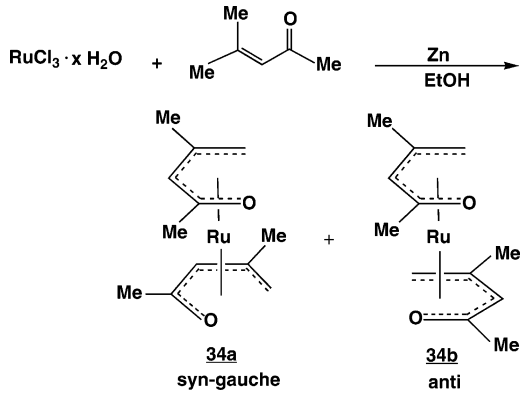
(17) Kloosterziel, H.; Heiszwolf, G. J. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 807.

(18) Kloosterziel also reported the synthesis of a sickle-shaped oxapentadienide from the base-induced electrocyclic opening of 2,5-dihydrofuran: Kloosterziel, H.; Van Drunnen, J. A. A.; Galama, P. *J. Chem. Soc., Chem. Commun.* **1969**, 885.

Scheme 15



Scheme 16

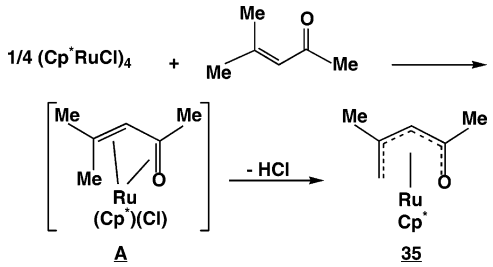


No C−H bond activation or metallacycle formation was observed in any of these oxapentadienyl−rhodium systems.

E. Oxapentadienyl−Metal Complexes from Reactions Involving Enones and Enals. The first homoleptic oxapentadienyl−metal complex was reported in 1991 by Schmidt.[21] As shown in Scheme 16, treatment of $RuCl_3 \cdot xH_2O$ with mesityl oxide in the presence of zinc as a reducing agent produced an "open" ruthenocene, (η^5-2,4-dimethyl-5-oxapentadienyl)$_2$Ru, as two stereoisomers, **34a**,**b**, both of which were characterized by X-ray diffraction. In each case, the ligands were almost planar and resided essentially parallel to one another. There was no NMR spectroscopic evidence for solution-phase rotation of the oxapentadienyl ligands with respect to one another.

In 1992, Ernst[22] reported the synthesis of "half-open" ruthenocenes containing oxapentadienyl and cyclopentadienyl ligands. In a typical reaction, $(Cp^*RuCl)_4$ was treated with mesityl oxide in the presence of a mild base (K_2CO_3), leading to the production of (η^5-2,4-dimethyl-5-oxapentadienyl)Ru(Cp*) (**35**; Scheme 17). Mechanistically, this reaction is thought to proceed by loss of HCl from an (η^4-enone)Ru(Cp*)(Cl) intermediate (**A**; Scheme 17).

Scheme 17



Similarly, the use of 2-methyl-2-pentenal led to the formation of (η^5-1,3-dimethyl-5-oxapentadienyl)Ru(Cp*). However, less substituted enals or enones did not lead to the desired products. Instead, scission of a carbon−carbon bond occurred, leading to carbonyl extrusion and coordination of the remaining organic fragment as a ligand.[23]

F. Half-Open Metallocenes from Anionic Oxapentadienide Reagents. Recently, Paz-Sandoval[24] reported that half-open ruthenocenes can also be conveniently synthesized by using preformed anionic oxapentadienide reagents. In a typical reaction, lithium 2,4-dimethyl-5-oxapentadienide was reacted with $(Cp^*RuCl)_4$ to produce (η^5-2,4-dimethyl-5-oxapentadienyl)Ru(Cp*) (**35**). As shown in Scheme 18, treatment of **35** with various phosphines or CO (L) led to $\eta^5 \rightarrow \eta^3$ oxapentadienyl rearrangement and production of (*syn*-(1,2,3-η)-2,4-dimethyl-5-oxapentadienyl)Ru(Cp*)(L) (**36**).[25] Compound **35** also readily underwent oxidative addition with I_2, $CHCl_3$, and $SnCl_4$, producing **37**−**39**[26] (Scheme 18), respectively. Similarly, treatment of **35** with O_2 produced the η^2-peroxo compound **40**. In general, the kinetic products of these oxidative addition reactions possessed *anti*-1,2,3-η-oxapentadienyl ligands (as shown), but in some cases the *syn* isomers appeared over time.

A comparison of the reactivity of **35** to that of the analogous *pentadienyl* complex (η^5-2,4-dimethylpentadienyl)Ru(Cp*) led to the conclusion that while oxapentadienyl complexes undergo reactions similar to those of their all-carbon analogues, they are generally *more* reactive due to the weaker coordination of the C−O π-bond.

Paz-Sandoval[27] also recently reported the syntheses of half-open iridocenium and rhodocenium complexes containing 2,4-dimethyl-5-oxapentadienyl and pentamethylcyclopentadienyl ligands. While the iridium compound **6** was previously reported by Maitlis (cf. Scheme 4), Paz-Sandoval's approach utilized an anionic oxapentadienide reagent, lithium 2,4-dimethyl-5-oxapentadienide, as shown in Scheme 19. Note that, in these syntheses, the η^3-oxapentadienyl complexes ((1,2,3-η)-2,4-dimethyl-5-oxapentadienyl)M(Cp*)(Cl) (**41**, M = Ir; **42**, M = Rh) served as intermediates and that the half-open iridocenium (**6**) was produced together with [(η^5-2-methyl-4-hydroxypentadienyl)Ir(Cp*)]$^+PF_6^-$ (**7**), the enol form of **6**.

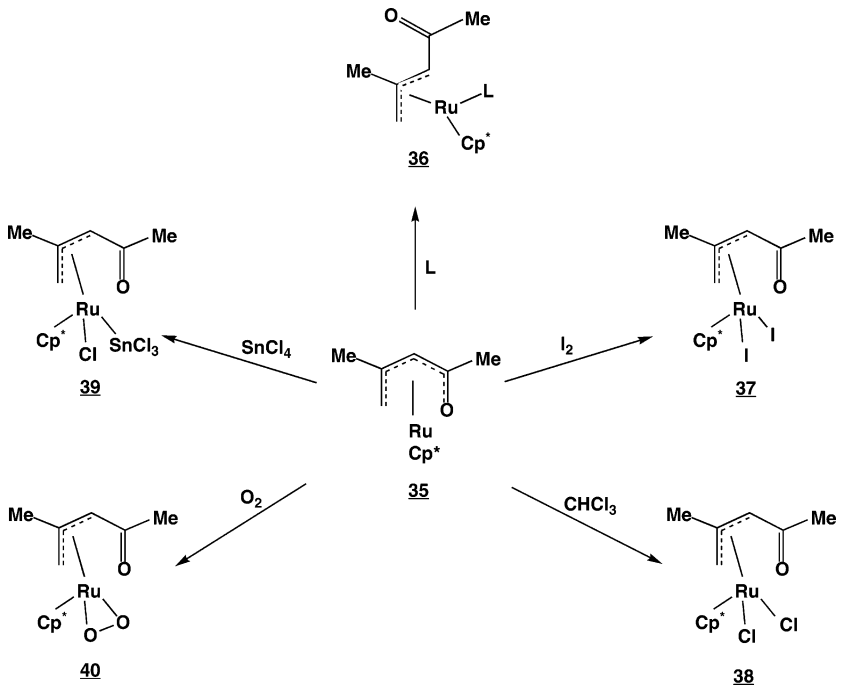
Both **6** and **43** readily added phosphine ligands (L), including PMe_3 and PPh_3, to produce [((1,2,3-η)-2,4-dimethyl-5-oxapentadienyl)M(Cp*)(L)]$^+$ complexes (**44** and **45**; Scheme 20). In some of these reactions, there was strong NMR spectroscopic evidence for the intermediacy of a novel 1,5-η-oxapentadienyl species (**A**; Scheme 20). These phosphine addition reactions proceeded more readily than those involving half-open ruthenocene (**35**),

(19) (a) Bleeke, J. R.; Haile, T.; Chiang, M. Y. *Organometallics* **1991**, *10*, 19. (b) Bleeke, J. R.; Haile, T.; New, P. R.; Chiang, M. Y. *Organometallics* **1993**, *12*, 517. (c) The solution-phase geometries of these methylated anions have not yet been firmly established. (d) Bleeke, J. R.; Haile, T. Previously unpublished results. (e) Bleeke, J. R.; New, P. R.; Blanchard, J. M. B.; Haile, T.; Beatty, A. M. *Organometallics* **1995**, *14*, 5127.

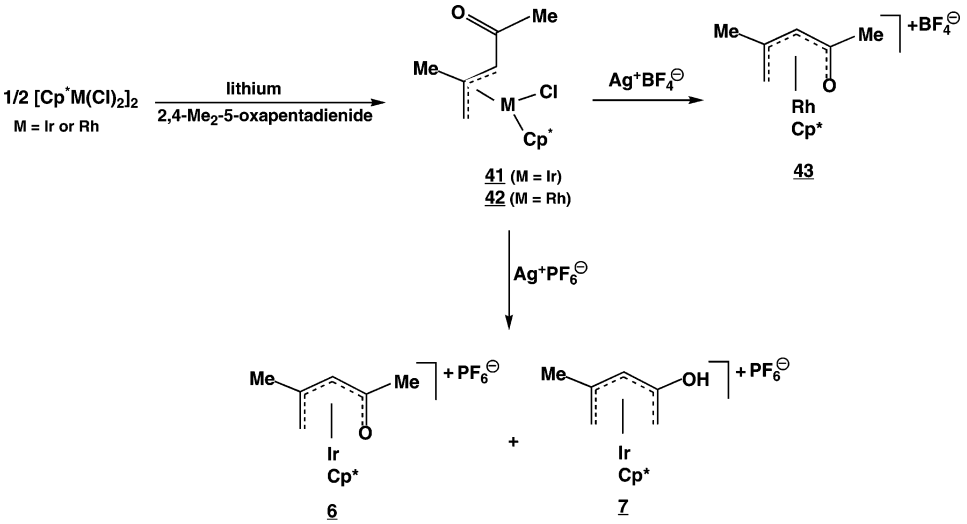
(20) Bleeke, J. R.; Donnay, E.; Rath, N. P. *Organometallics* **2002**, *21*, 4099.

(21) Schmidt, T.; Goddard, R. *J. Chem. Soc., Chem. Commun.* **1991**, 1427.

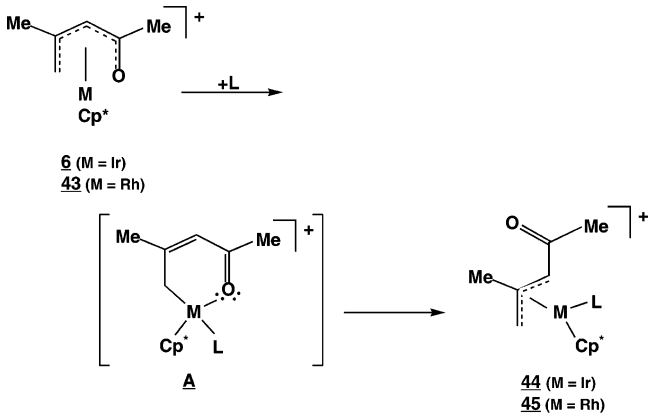
Scheme 18



Scheme 19



Scheme 20

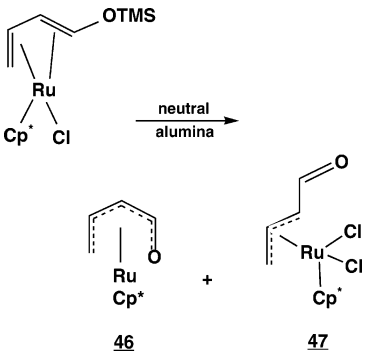


probably due to the positive charges on the Rh and Ir centers. In fact, even acetonitrile, normally a relatively weak ligand, added reversibly to the metal centers in both **6** and **43**. However, unlike **35**, compounds **6** and **43** did not undergo clean oxidative addition reactions with substrates such as $SnCl_4$ and I_2. Instead, these reactions led to loss of the oxapentadienyl ligands and the production of various M(III) decomposition products.

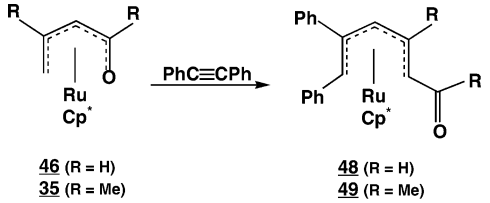
G. Oxapentadienyl−Metal Complexes from ((Trimethylsilyl)oxy)butadiene−Metal Precursors (Revisited). As discussed earlier (section IIB), Green[5] originally introduced the methodology of using ((trimethylsilyl)oxy)butadiene as a precursor ligand for oxapentadienyl.[28] Recently, this synthetic approach has been embraced by a new group of researchers and applied to a larger set of transition metals. For example, Murai[29] produced the unmethylated oxapentadienyl complex [((1,2,3-η)-5-oxapentadienyl)Pd(Cl)]$_2$, in quantitative yield by treating $Pd(Cl)_2(NCMe)_2$ with ((trimethylsilyl)oxy)-butadiene. Söderberg[30] greatly expanded the scope of

(22) Trakarnpruk, W.; Arif, A. M.; Ernst, R. D. *Organometallics* **1992**, *11*, 1686.

Scheme 21



Scheme 22

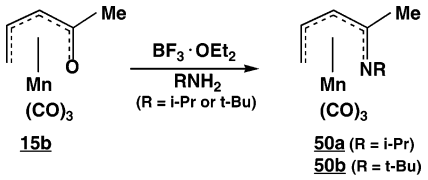


this reaction and produced a large family of [((1,2,3-η)-5-oxapentadienyl)Pd(Cl)]$_2$ complexes with a variety of alkyl substituents on the oxapentadienyl ligands.

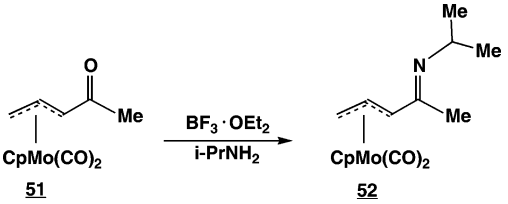
Very recently Paz-Sandoval[31] used a ((trimethylsilyl)oxy)butadiene precursor, (η^4-1-((trimethylsilyl)oxy)-butadiene)Ru(Cp*)(Cl), to produce a half-open ruthenocene containing the unmethylated oxapentadienyl ligand, (η^5-oxapentadienyl)Ru(Cp*) (**46**; Scheme 21). Compound **46** was obtained from the precursor via a disproportionation reaction, which also produced ((1,2,3-η)-5-oxapentadienyl)Ru(Cp*)(Cl)$_2$ (**47**) as the other product. The isolation of **46** was significant, in that earlier attempts to produce half-open ruthenocenes containing the unmethylated oxapentadienyl ligand led to carbon–carbon bond scission and CO extrusion (vide supra).

Paz-Sandoval[31] has investigated the rich reaction chemistry of half-open ruthenocene **46** and its dimethylated analogue, **35**, with alkynes. As shown in Scheme 22, when **46** and **35** were treated with diphenylacetylene, pentadienyl compounds **48** and **49**, respectively,

Scheme 23



Scheme 24



were produced by insertion of the alkyne into the Ru–C1 bond. Interestingly, the pentadienyl analogue of **35**, (2,4-dimethylpentadienyl)Ru(Cp*), did not react with diphenylacetylene even under forcing conditions.

III. Azapentadienyl–Metal Complexes

A. Azapentadienyl–Metal Complexes from Oxapentadienyl–Metal Precursors. The first azapentadienyl–metal complexes were prepared from oxapentadienyl–metal precursors. In 1990, Liu[12] reported that treatment of (η^5-4-methyl-5-oxapentadienyl)Mn(CO)$_3$ (**15b**) with BF_3·OEt_2, followed by addition of RNH_2 (R = i-Pr, t-Bu), generated (η^5-4-methyl-5-R-5-azapentadienyl)Mn(CO)$_3$ (**50**; see Scheme 23). It is not known if the nucleophilic attack of the amine occurred directly on C4 of the η^5-oxapentadienyl ligand or whether an $\eta^5 \rightarrow \eta^3$ ligand shift preceded the attack.

Rotation of the η^5-azapentadienyl ligand with respect to the Mo(CO)$_3$ moiety was studied by variable-temperature ^{13}C NMR spectroscopy, and the rotational barrier was determined to be 16.9 kcal/mol for **50a** and 17.3 kcal/mol for **50b**. This compares to a value of 15.8 kcal/mol for the η^5-oxapentadienyl precursor **15b**.

While oxapentadienyl precursor **15b** was reactive toward phosphine addition at manganese (vide supra), the azapentadienyl complexes **50a**,**b** did not undergo phosphine addition or substitution, even in cyclohexane at reflux. This lack of reactivity may reflect stronger bonding of the C=NR moiety to the metal center (as compared to the C=O group) and, hence, less of a tendency to undergo the $\eta^5 \rightarrow \eta^3$ shift.

In a similar vein, Liu[13] showed that treatment of ((1,2,3-η)-4-methyl-5-oxapentadienyl)Mo(Cp)(CO)$_2$ (**51**) with BF_3·OEt_2 and i-$PrNH_2$ led to the production of ((1,2,3-η)-4-methyl-5-isopropyl-5-azapentadienyl)Mo(Cp)-(CO)$_2$ (**52**) (see Scheme 24). The pure *syn* isomer of **51** was used in this reaction and, not surprisingly, the *syn* geometry of the oxapentadienyl ligand was retained in the azapentadienyl product, **52**. Treatment of **52** with HBF_4·Et_2O led to protonation at nitrogen and production of the corresponding iminium salt.

B. Azapentadienyl–Metal Complexes from Anionic Azapentadienide Reagents and Metal Halides. My research group[32] first became involved in the area of azapentadienyl–metal chemistry in 1993. Be-

(23) Trakarnpruk, W.; Arif, A. M.; Ernst, R. D. *Organometallics* **1994**, *13*, 2423.

(24) Clemente, M. E. N.; Saavedra, P. J.; Vásquez, M. C.; Paz-Sandoval, M. A.; Arif, A. M.; Ernst, R. D. *Organometallics* **2002**, *21*, 592. See also: Navarro, M. E.; Cházaro, L. F.; Gonzáles, F. J.; Paz-Sandoval, M. A. *J. Electroanal. Chem.* **2000**, *480*, 18.

(25) Close analogues of these compounds, (*syn*-(1,2,3-η)-5-oxapentadienyl)-Ru(Cp*)(L) (L = PPh_3, CH_2=CH_2, PhCH=CH_2, PhCCPh), were previously prepared by Koelle via dehydrogenative rearrangement of the butenyloxy ligands in butenyloxy–ruthenium precursors. See: Koelle, U.; Kang, B.-S.; Thewalt, U. *Organometallics* **1992**, *11*, 2893.

(26) A close relative of compound **38**, (*anti*-(1,2,3-η)-5-oxapentadienyl)-Ru(Cp*)(Br)$_2$, was previously prepared from the reaction of (η^4-1-methoxybutadiene)Ru(Cp*)(Br) with Br_2. See: Gemel, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 532.

(27) Salas, I. I. R.; Paz-Sandoval, M. A.; Nöth, H. *Organometallics* **2002**, *21*, 4696.

(28) For a recent, related contribution from the Green group, see: Beddows, C. J.; Box, M. R.; Butters, C.; Carr, N.; Green, M.; Kursawe, M.; Mahon, M. F. *J. Organomet. Chem.* **1998**, *550*, 267.

(29) Ogoshi, S.; Hirako, K.; Nakanishi, J.; Ohe, K.; Murai, S. *J. Organomet. Chem.* **1993**, *445*, C13. For a related reaction, see: Ogoshi, S.; Ohe, K.; Chatani, N.; Kurosawa, H.; Murai, S. *Organometallics* **1991**, *10*, 3813.

(30) Söderberg, B. C.; Berry, A. K.; Jones, P. C. *Organometallics* **1998**, *17*, 1069.

(31) Sánchez-Castro, M. E.; Ramirez-Monroy, A.; Paz-Sandoval, M. A. *Organometallics* **2005**, *24*, 2875.

(32) Bleeke, J. R.; Luaders, S. T.; Robinson, K. D. *Organometallics* **1994**, *13*, 1592.

Scheme 25

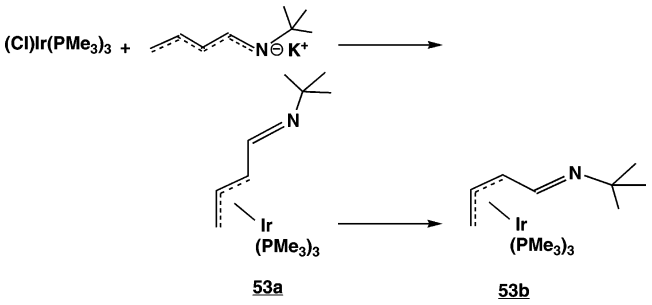
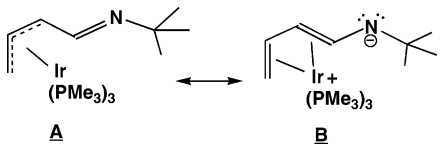


Chart 2



cause of our earlier success with anionic oxapentadienide (and anionic pentadienide) reagents, we chose to apply a similar methodology to the synthesis of azapentadienyl−metal complexes. By reacting *tert*-butylazapentadiene with potassium amide in liquid ammonia, we were able to produce and isolate potassium *tert*-butylazapentadienide. This species exhibited NMR spectra that were identical with the lithium analogue reported earlier by Würthwein[33] and were consistent with its formulation as a W-shaped *E*,*E* isomer.

Treatment of (Cl)Ir(PMe_3)$_3$ with potassium *tert*-butylazapentadienide led to the immediate formation of (*syn*-(1,2,3-η)-5-*tert*-butyl-5-azapentadienyl)Ir(PMe_3)$_3$ (**53a**; Scheme 25). This reaction apparently involved initial nucleophilic attack by the *carbon* end of the *tert*-butylazapentadienide reagent on iridium and, in this way, differed from the analogous reaction involving oxapentadienide (vide supra), where initial attack by oxygen was observed. Most likely, this reversal in the site of reaction resulted from the presence of the bulky *tert*-butyl substituent on nitrogen rather than from a decrease in the nucelophilicity of the heteroatom.

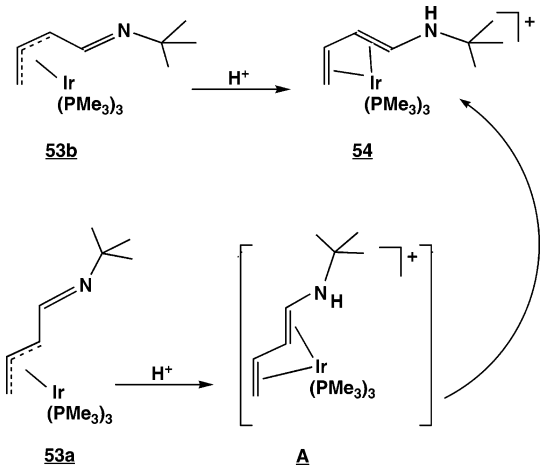
While **53** was initially formed as the *syn* isomer (**53a**), it slowly (several hours at room temperature) converted to the thermodynamically favored *anti* isomer (**53b**). The thermodynamic preference for the *anti* isomer may result from resonance stabilization provided by the η^4-*s*-*cis*-butadiene resonance structure (**B** in Chart 2). Note that, in this resonance structure, the formal negative-charge resides on the most electronegative atom, nitrogen, while the formal positive charge is localized on iridium, where it can be effectively neutralized by the PMe_3 ligands.

Protonation of **53b** with H^+OTf^- occurred at nitrogen and led to the clean production of the η^4-*s*-*cis*-*tert*-butylaminobutadiene complex **54** (Scheme 26). Interestingly, protonation of the *syn* isomer **53a** yielded primarily the same product, presumably through the intermediacy of the transient η^4-*s*-*trans*-*tert*-butylaminobutadiene complex (**A**; Scheme 26). Further addition of acid to **54** led to a second protonation at nitrogen, generating the corresponding ammonium salt.

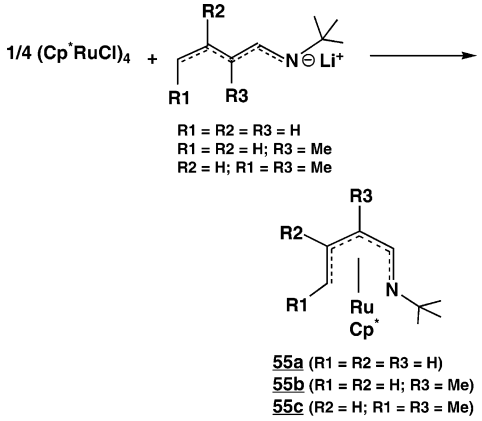
C. Azapentadienyl−Ruthenium Complexes from Anionic Azapentadienide or Group 14 Enimine

(33) Wolf, G.; Würthwein, E.-U. *Chem. Ber.* **1991**, *124*, 889.

Scheme 26



Scheme 27



Reagents. In 1999, Paz-Sandoval and Ernst[34] reported the synthesis of a series of half-open ruthenocenes containing *tert*-butylazapentadienyl and pentamethylcyclopentadienyl ligands. In these reactions, (Cp*RuCl)$_4$ was treated with various lithium *tert*-butylazapentadienide reagents[35] to produce the desired compounds, **55a**−**c** (see Scheme 27).

The group 14 enimine derivatives Me_3MCH(R1)C(R2)=C(R3)CH=NCMe$_3$ (M = Si, Ge, Sn), were also investigated as reagents[35] for introducing the azapentadienyl ligand onto the ruthenium center. These reactions tended to be a bit more complicated than those involving the lithium reagents, leading to mixtures of products **55**−**57** (see Scheme 28), with yields depending on the group 14 metal, the methylation pattern of the azapentadienyl, and the reaction solvent. For example, the η^5-azapentadienyl complexes **55** were always favored when the tin enimine reagents were used, while the η^3 complex **57a** (R1 = R2 = R3 = H) was strongly favored when the silicon enimine reagent was employed and the reaction solvent was THF.

Crystal structures of **55a**−**c** were obtained, and they represent the first X-ray structure determinations of η^5-azapentadienyl−metal complexes. In each structure, the five azapentadienyl atoms were strongly coordinated to ruthenium and the ligand was essentially planar. Small differences in C−C bond lengths led to the conclusion that resonance structure **A** (Chart 3) may dominate for methyl-substituted **55b**,**c** while resonance structure **B** may be more important for unsubstituted **55a**.

Scheme 28

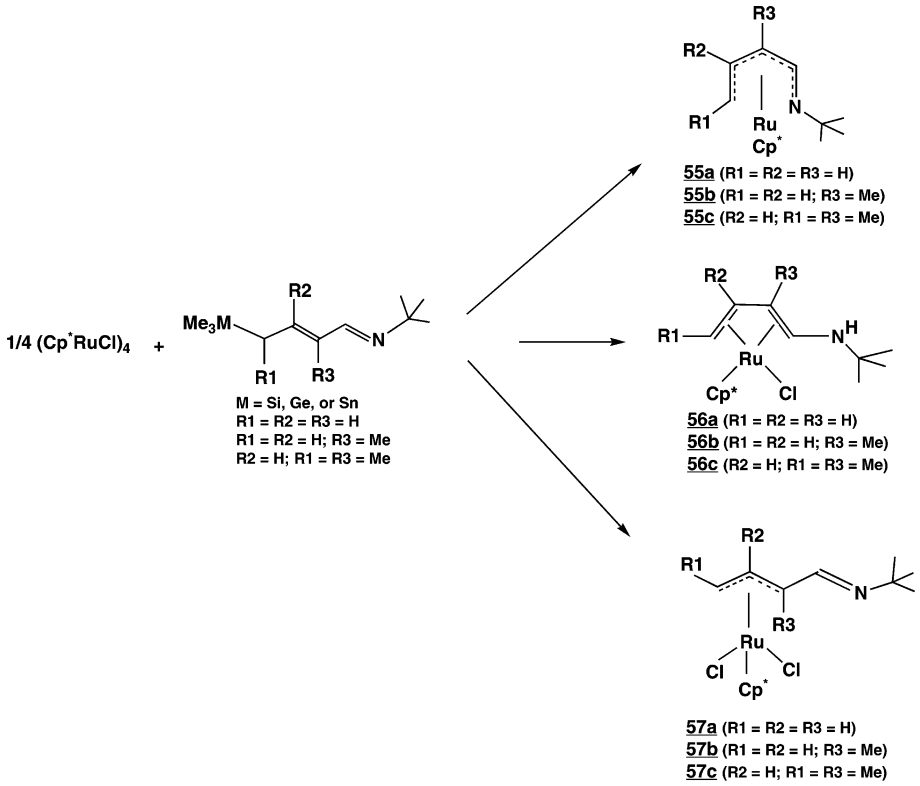
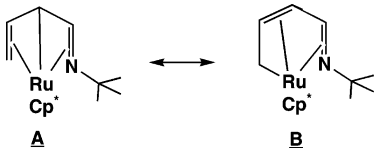
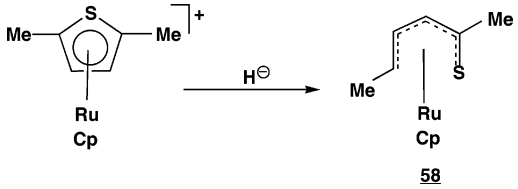


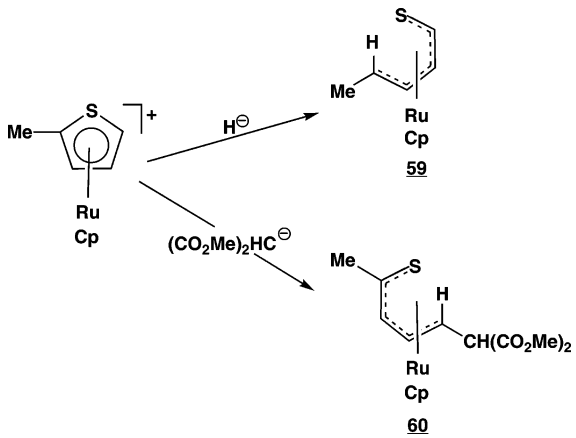
Chart 3



Scheme 29



Scheme 30



IV. Thiapentadienyl−Metal Complexes

A. Thiapentadienyl−Metal Complexes from Nucleophilic Addition to Thiophene Ligands. The first example of a thiapentadienyl−metal complex, (η^5-1,4-dimethyl-5-thiapentadienyl)Ru(Cp) (**58**), was reported by Angelici[36] in 1987 and resulted from the reaction of a cationic thiophene complex, [(η^5-2,5-dimethylthiophene)-Ru(Cp)]$^+$, with hydride, as shown in Scheme 29. The thiapentadienyl ligand was formed by nucleophilic addition of hydride at a carbon adjacent to sulfur, followed by C−S bond cleavage. Although the X-ray crystal structure of **58** was slightly disordered, it clearly showed the half-open sandwich structure.

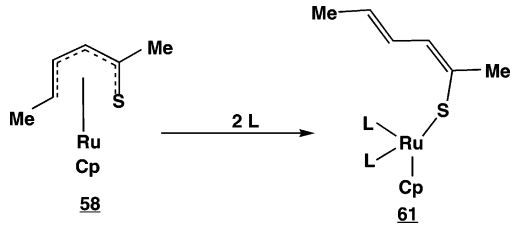
Angelici demonstrated the generality of this approach by using thiophene precursors with a variety of methylation patterns and a variety of nucleophiles, including $(CO_2Me)_2HC^-$, EtS^-, and MeO^-. [37] Interestingly, when [(η^5-2-methylthiophene)Ru(Cp)]$^+$ was treated with hydride (H^-) and with malonate ($(CO_2Me)_2HC^-$), nucleophilic attack occurred at different sites. As shown in Scheme 30, hydride attack (and ring opening) occurred at the methylated carbon, producing **59**, while the bulky malonate added at the unmethylated carbon adjacent to sulfur, producing **60**. Note also that in **59**, the added hydride is situated "endo" (in a *Z* site) while the malonate in **60** is "exo" (in an *E* site).

Treatment of η^5-thiapentadienyl complex **58** with 2e ligands (L), including PPh_2Me or CO, led to displacement of the butadiene moiety and production of (5-η-1,4-dimethyl-5-thiapentadienyl)Ru(Cp)(L)$_2$ (**61**; Scheme 31).

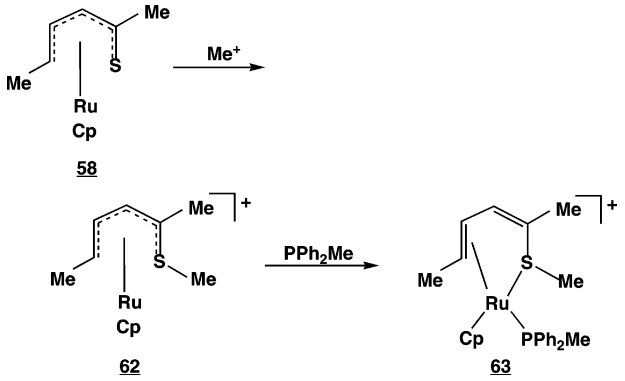
As shown in Scheme 32, treatment of the η^5-thiapentadienyl complex **58** with an electrophilic reagent,

(34) Gutiérrez, J. A.; Clemente, M. E. N.; Paz-Sandoval, M. A.; Arif, A. M.; Ernst, R. D. *Organometallics* **1999**, *18*, 1068.
(35) Gutiérrez, J. A.; Paz-Sandoval, M. A.; Robles, J. *J. Organomet. Chem.* **2000**, *599*, 147.
(36) Hachgenei, J. W.; Angelici, R. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 909.
(37) (a) Hachgenci, J. W.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *355*, 359. (b) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897.

Scheme 31



Scheme 32



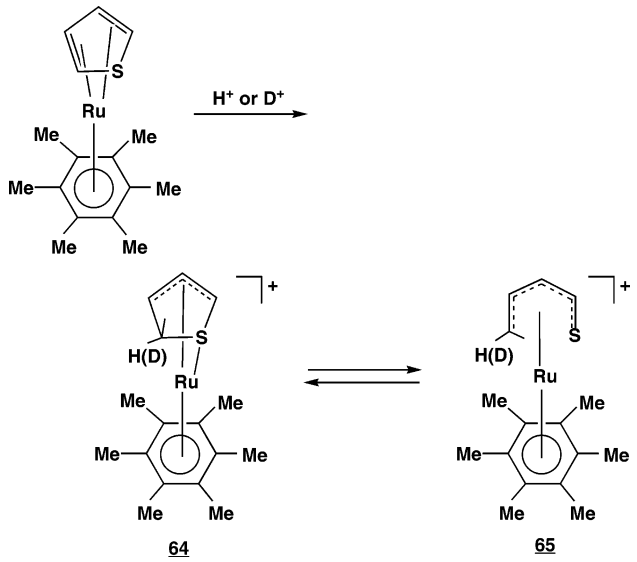
Me_3O^+, led to methylation at sulfur and production of $[(\eta^5\text{-}1,4,5\text{-trimethyl-5-thiapentadienyl})Ru(Cp)]^+$ (**62**). When **62** was reacted with PPh_2Me, the internal double bond C3−C4 was displaced from the metal center and thioether complex **63** was produced. Two isomers of **63** were evident from the NMR spectrum, probably resulting from two possible positions (up or down) for the methyl group on sulfur. Treatment of **63** with additional phosphine led to total displacement of the thioether.

B. A Thiapentadienyl−Metal Complex from Electrophilic Addition to a Thiophene Ligand. In an approach complementary to that of Angelici, Rauchfuss[38] showed that *protonation* of a metal-bound thiophene ligand led to C−S bond scission and formation of a thiapentadienyl−metal complex. As shown in Scheme 33, treatment of (η^4-thiophene)Ru(η^6-C_6Me_6) with weak acids (e.g., NH_4^+) produced the allyl−thioether complex **64** via protonation at Ru, followed by hydride migration to the endo side of the thiophene ring. In acetone solution (and even in the solid state), compound **64** underwent reversible C−S bond cleavage to establish an equilibrium with (η^5-thiapentadienyl)Ru(η^6-C_6Me_6) (**65**; K_{eq} = 4.38 at 45 °C in acetone). Ring opening was stereospecific; hence, protonation with D^+ led to deuterium incorporation exclusively into the endo site of **64** and the exo (or *E*) site of **65** (as shown in Scheme 33).

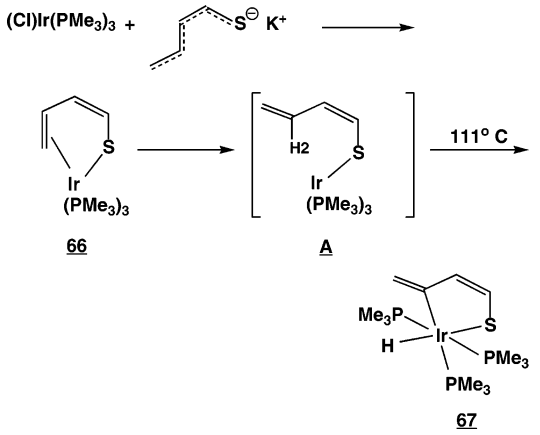
While the 2,5-dimethylthiophene and tetramethylthiophene analogues of **64** could be synthesized, these species did not undergo the C−S cleavage reaction to generate thiapentadienyl−Ru products.

C. Thiapentadienyl−Metal Complexes from Anionic Thiapentadienide Reagents and Metal Halides. As with the oxapentadienyl−metal and azapentadienyl−metal chemistry described earlier, we chose to synthesize thiapentadienyl−metal complexes using

Scheme 33



Scheme 34



anionic thiapentadienide reagents. Kloosterziel[39] had previously reported the synthesis of potassium thiapentadienide from the ring-opening reaction of 2,5-dihydrothiophene with potassium amide in liquid ammonia. On the basis of the ^1H NMR coupling constants, the thiapentadienide anion was proposed to have a sickle shape in solution.

We reproduced the Kloosterziel synthesis, isolated potassium thiapentadienide as an off-white powder, and reacted it with (Cl)Ir(PMe_3)$_3$. This reaction, which we reported in 1992,[40] led cleanly to the production of ((1,2,5-η)-5-thiapentadienyl)Ir(PMe_3)$_3$ (**66**; Scheme 34). Unlike its oxapentadienyl analogue **19**, compound **66** did *not* undergo a (1,2,5-η)- to (1,2,3-η)-thiapentadienyl ligand shift. However, upon heating in toluene at reflux (111 °C), C−H2 bond activation occurred, producing the metallathiacyclopentene **67**.

Treatment of **66** with Me^+ (from MeOTf) or with H^+ (from $HBF_4{\cdot}OEt_2$) led to electrophilic attack at two different sites (see Scheme 35).[41] Me^+ attacked the sulfur center to produce **68**, an analogue of Angelici's

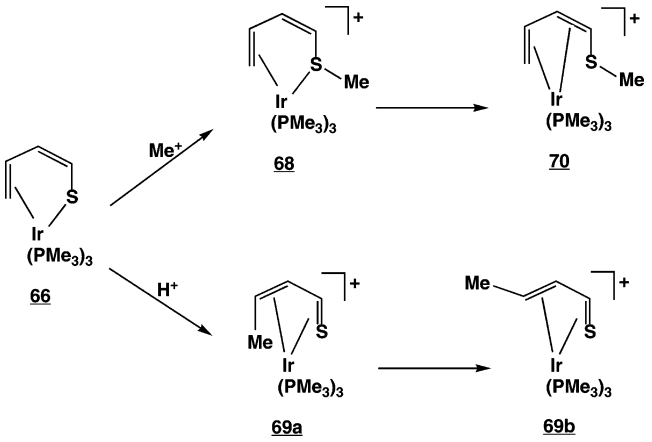
(38) (a) Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8515. (b) Luo, S.; Rauchfuss, T. B.; Gan, Z. *J. Am. Chem. Soc.* **1993**, *115*, 4943.

(39) Kloosterziel, H.; Van Drunen, J. A. A.; Galama, P. *J. Chem. Soc., Chem. Commun.* **1969**, 885.

(40) Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740.

(41) Bleeke, J. R.; Ortwerth, M. F.; Rohde, A. M. *Organometallics* **1995**, *14*, 2813.

Scheme 35



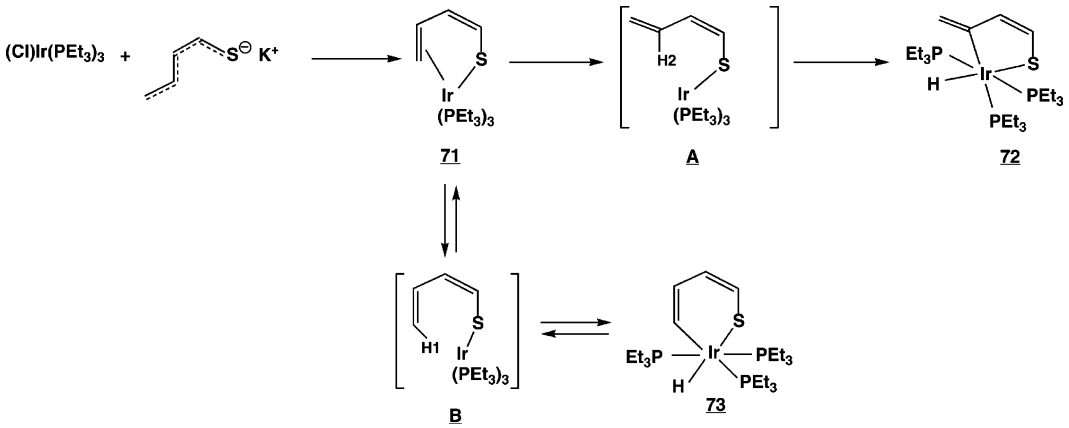
compound **63**, while H^+ added to C1 to produce an η^4-thiapentadiene complex, **69a**. The *initial* site of H^+ attack was not established but could be C1, Ir, or even S. As shown in Scheme 35, both **68** and **69a** underwent rearrangements over time.

The reaction of $(Cl)Ir(PEt_3)_3$ with potassium thiapentadienide was very similar to that described above for the tris(PMe_3) system.[40,41] ((1,2,5-η)-thiapentadienyl)-$Ir(PEt_3)_3$ (**71**; Scheme 36) was the kinetic product of the reaction, but in this case, C−H2 bond activation occurred at room temperature to generate the iridathiacyclopentene product **72**. In this system, the six-membered metallacycle (**73**; Scheme 36), produced via C−H1 activation, was also observed by NMR spectroscopy, but it gradually converted to the favored five-membered ring (**72**). A *stable* six-membered ring was obtained from the reaction of lithium 2,3-dimethyl-5-thiapentadienide with $(Cl)Ir(PEt_3)_3$.[42] Here, C−H2 activation was blocked by the presence of a methyl group at C2 and, hence, C−H1 activation was favored.

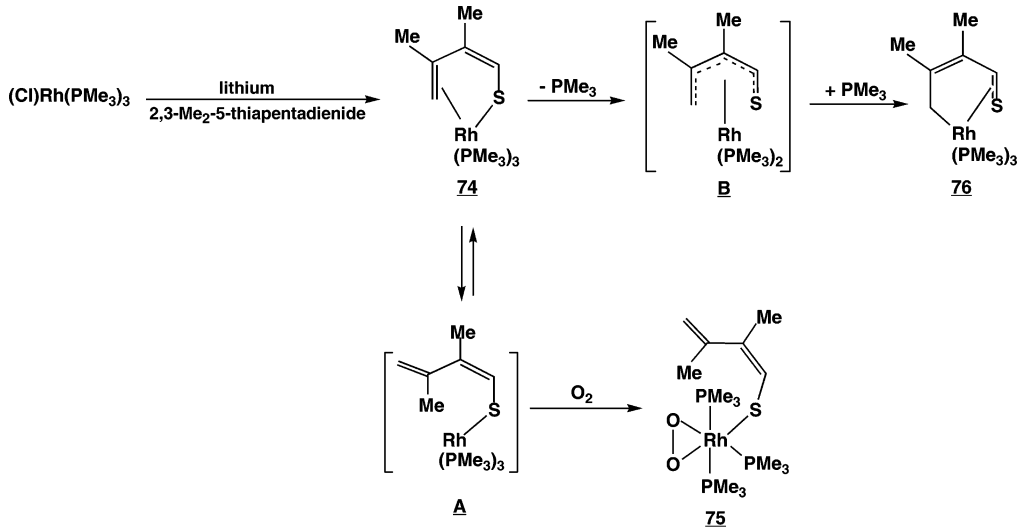
Recently, we have expanded our study of thiapentadienyl−metal chemistry to include rhodium.[43a] As shown in Scheme 37, treatment of $(Cl)Rh(PMe_3)_3$ with lithium 2,3-dimethyl-5-thiapentadienide[43b] led to the production of ((1,2,5-η)-2,3-dimethyl-5-thiapentadienyl)$Rh(PMe_3)_3$ (**74**). In solution at room temperature, **74** underwent a reversible dissociation of the double bond C1−C2, producing the η^1-thiapentadienyl intermediate **A**, which could be "trapped" by reaction with oxygen (compound **75**). Upon stirring at room temperature, **74** gradually (48 h) converted to ((1,4,5-η)-2,3-dimethyl-5-thiapentadienyl)$Rh(PMe_3)_3$ (**76**), probably via the η^5-thiapentadienyl intermediate **B**. Unlike the iridium chemistry described above, there was no evidence for C−H bond activation and metallacycle formation, even upon heating.

The reaction of $(Cl)Rh(PEt_3)_3$ with lithium 2,3-dimethyl-5-thiapentadienide took a similar pathway,[43] but in this case the kinetic product was a ground-state η^1-

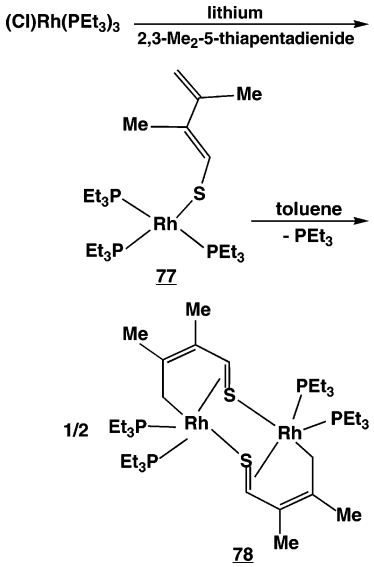
Scheme 36



Scheme 37



Scheme 38



thiapentadienyl complex, **77** (Scheme 38), due to the greater steric bulk of PEt_3 as compared to PMe_3. Like its PMe_3 analogue (**74**), compound **77** also isomerized to a (1,4,5-η)-5-thiapentadienyl product when stirred in toluene, but this isomerization was accompanied by dimerization, leading to the sulfur-bridged product **78**.

Interestingly, a second sulfur-bridged dimer (**79**; Scheme 39) was obtained when **77** was stirred in the coordinating solvent, acetone. In this product, the thiapentadienyl ligands remained coordinated to rhodium in an η^1 mode and were W-shaped with *trans* internal double bonds. Treatment of **79** with PEt_3 regenerated the monomer, **77**, suggesting that the η^1-thiapentadienyl ligand in **77** was W-shaped as well.

D. Thiapentadienyl−Metal Complexes from Thiophene-Derived Metallacycles. A major contribution to thiapentadienyl−metal chemistry has been made by Bianchini and co-workers, who reported their work in a series of papers beginning in 1993.[44] As shown in Scheme 40, Bianchini found that treatment of the η^4-benzene complex [(η^4-benzene)Ir(triphos)]$^+$ with thiophene led to C−S bond activation and production of iridathiabenzene **80**. Further treatment with hydride led to iridathiacyclohexadiene hydride **81**, which rearranged to ((1,2,5-η)-5-thiapentadienyl)Ir(triphos) (**82**), a close relative of our compound, **66**. The conversion of **81** to **82** can be viewed as a reductive elimination of hydride and vinyl ligands.

Compound **82** was also prepared in a more straightforward way by treatment of (Et)$(H)_2$Ir(triphos) with thiophene in THF at reflux. In this reaction, one of the hydride ligands was reductively eliminated with the ethyl group to generate a reactive 16e iridium species, (H)Ir(triphos), which bound the thiophene (probably through the sulfur center) and then inserted into a C−S bond to produce the iridathiacyclohexadiene hydride complex (**81**). Migration of the metal hydride to C1 of the metallacycle produced **82**. Similarly, the reaction of (Et)$(H)_2$Ir(triphos) with benzo[*b*]thiophene led to an analogue of **82**, containing a benzene ring fused to C3−C4 of the (1,2,5-η)-5-thiapentadienyl ligand.[45]

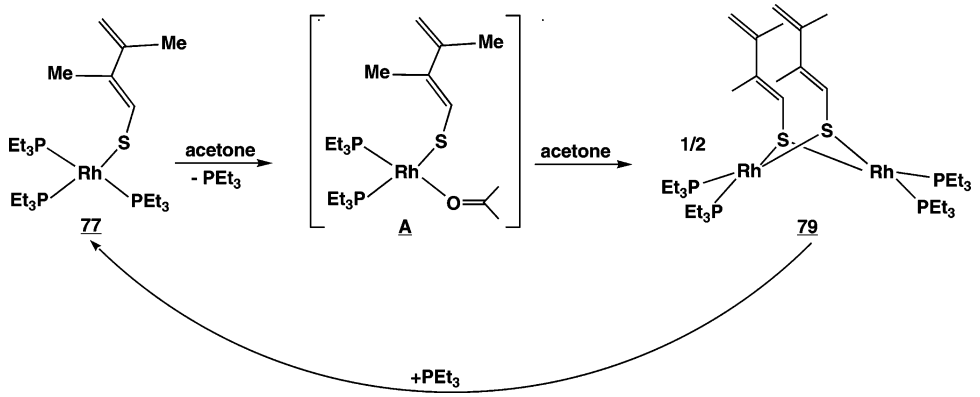
The reactivity of **82** toward electrophiles was similar to that described earlier for **66** (cf. Scheme 35). In particular, the reaction of **82** with methyl iodide resulted in methylation at sulfur and production of the thioether complex **83** (Scheme 41), while treatment with HBF_4·OEt_2 in the presence of CO led to proton addition at C1 and production of the η^2-thiapentadiene complex **84**. Interestingly, the nucleophilic sulfur center in **82** also coordinated to electrophilic metal fragments, including $M(CO)_5$ (M = Cr, Mo, W), generating heterobimetallic products.[46]

Bianchini demonstrated analogous chemistry in the rhodium system.[47] For example, treatment of $(H)_3$Rh(triphos) with thiophene, with benzo[*b*]thiophene, or with a variety of substituted thiophenes led to ((1,2,5-η)-5-thiapentadienyl)Rh(triphos) complexes (**85**; Scheme 42). The insertions involving substituted thiophenes were regioselective, always occurring exclusively at the C−S bond *away from* the substituent(s).

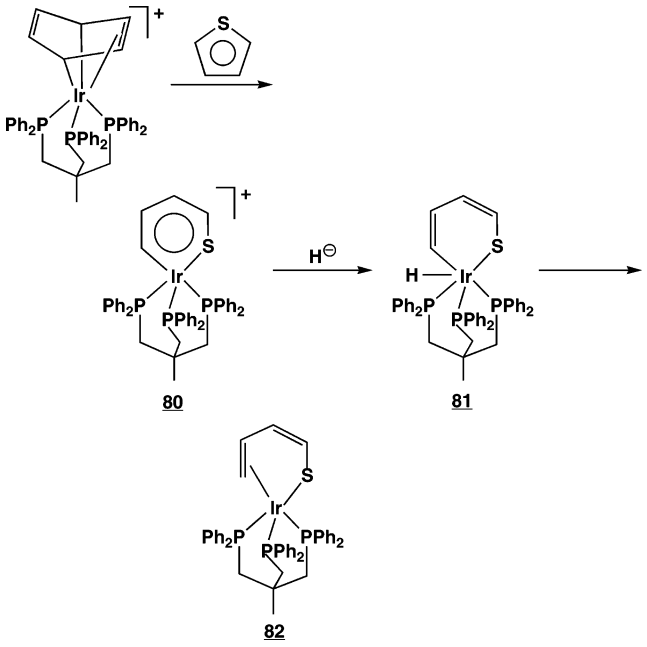
As shown in Scheme 42, the mechanism (by analogy to the iridium system) is believed to involve loss of H_2 from the rhodium precursor, S-coordination of the thiophene, oxidative addition across the thiophene C−S bond to form a metallathiacyclohexadiene hydride, and finally transfer of the metal hydride to C1 of the metallacycle. Studies of the competitive reactivity of various thiophenes showed that those with electron-withdrawing substituents were more reactive. This observation is consistent with the proposed mechanism in that the C−S bond activation involves electron donation from the metal center into the C−S antibonding orbital, and this electron flow is facilitated by electron-withdrawing groups in the thiophene.

The reactivity of ((1,2,5-η)-5-thiapentadienyl)Rh(triphos) (**85a**; R = R′ = H) toward electrophiles was studied in detail (see Scheme 43).[47a] As with the

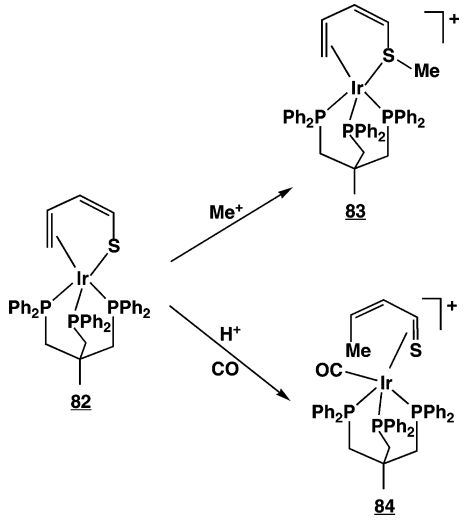
Scheme 39



Scheme 40



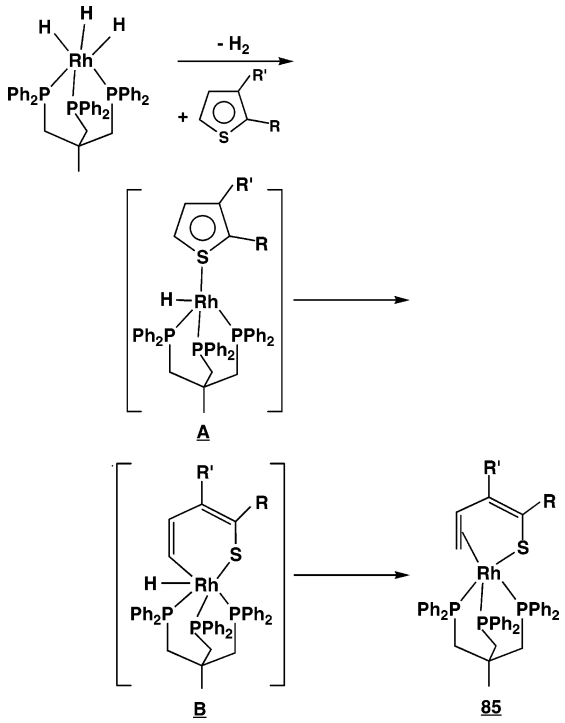
Scheme 41



analogous iridium complex (cf. Scheme 41), treatment with methyl iodide led to methylation at sulfur and production of thioether **86**, while treatment with $HBF_4 \cdot OEt_2$ resulted in protonation at C1 and production of an η^4-thiapentadiene complex, **87a**. Surprisingly, treatment of **85a** with trityl cation (CPh_3^+) led to electrophilic attack at C1 and production of a CPh_3-substituted η^4-thiapentadiene complex, **88**. The regiochemistry of this addition may be driven by steric effects—repulsion between the phenyl rings of the triphos ligand and of the trityl group. As with the iridium system, the electrophilic metal fragment $M(CO)_5$ (M = Cr, Mo, W) added to the nucleophilic sulfur center of **85a**, generating heterobimetallic products.[46]

It is interesting that Bianchini's ((1,2,5-η)-5-thiapentadienyl)Rh(triphos) complexes (**85**) showed no tendency to isomerize to the (1,4,5-η)-5-thiapentadienyl bonding mode. This is in marked contrast to our analogous compounds (cf. Schemes 37 and 38). A likely explanation

Scheme 42



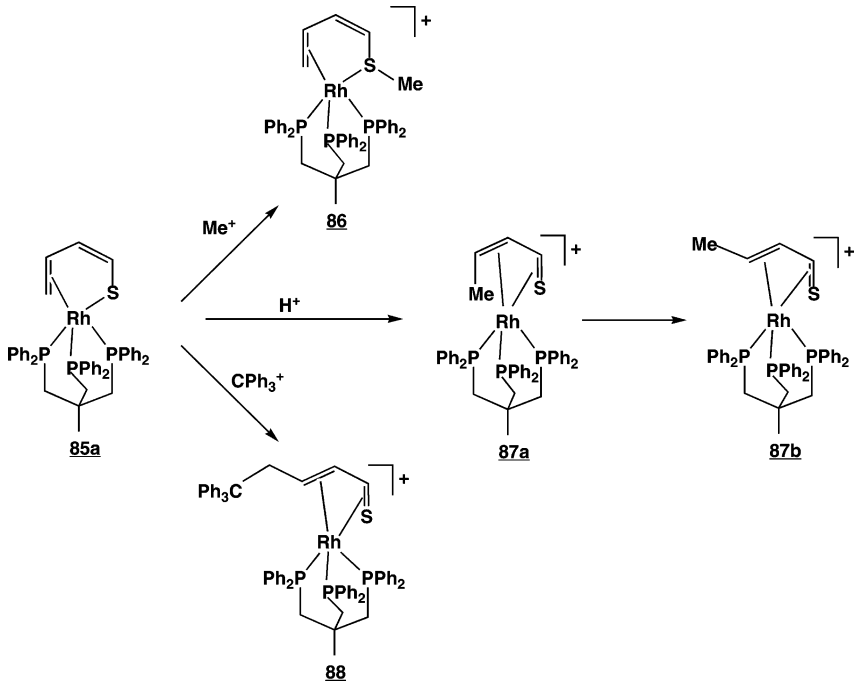
for this difference in behavior is that in our compounds, one of the monodentate PR_3 ligands can dissociate from the metal, allowing the thiapentadienyl ligand to adopt an η^5 bonding mode, a key step in the isomerization process. In Bianchini's complexes, on the other hand, the phosphine ligand is tridentate and more tightly bound to rhodium. In this case, the η^5-thiapentadienyl intermediate is inaccessible, and isomerization is therefore not observed.

E. μ_2-Thiapentadienyl−Metal Complex from a Thiophene-Derived Metallacycle. Recently, Hiraki and Onishi[48] reported the synthesis and structural characterization of a ruthenium dimer containing a novel μ_2,η^5-thiapentadienyl ligand. The reaction sequence, shown in Scheme 44, involved treatment of "$RuCO(PPh_3)_3$" with thiophene and led initially to **89a**, in which the phenyl group on the thiapentadienyl ligand had a *Z* orientation. When **89a** was treated with alumina or silica gel, it isomerized to the sterically favored *E* isomer, **89b**.

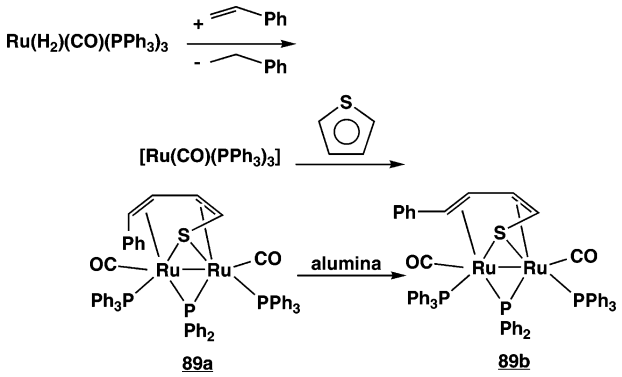
While the mechanism of formation for compound **89** is not known, it seems likely that C−S bond activation leads to a transient ruthenathiacyclohexadiene (**A**, Scheme 45), which then coordinates a second ruthenium center (**B**). Transfer of a phenyl group from PPh_3 to ruthenium (**D**) and then to C1 of the ruthenathiacyclohexadiene would produce **89a**.

(42) Bleeke, J. R.; Hinkle, P. V. *J. Am. Chem. Soc.* **1999**, *121*, 595.
(43) (a) Bleeke, J. R.; Wise, E. S.; Shokeen, M. *Organometallics* **2005**, *24*, 805. (b) The solution-phase geometry of the dimethylated anion has not yet been firmly established.
(44) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sanchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2731.
(45) Bianchini, C.; Jiménez, M. V.; Meli, A.; Moneti, S.; Vizza, F. *J. Organomet. Chem.* **1995**, *504*, 27.
(46) Bianchini, C.; Jiménez, M. V.; Meli, A.; Moneti, S.; Vizza, F. *Inorg. Chim. Acta* **1998**, *272*, 55.
(47) (a) Bianchini, C.; Frediani, P.; Herrera, V.; Jiménez, M. V.; Meli, A.; Rincón, L.; Sánchez-Delgado, R.; Vizza, F. *J. Am. Chem. Soc.* **1995**, *117*, 4333. (b) Bianchini, C.; Jiménez, M. V.; Meli, A.; Vizza, F. *Organometallics* **1995**, *14*, 3196. (c) Bianchini, C.; Jiménez, M. V.; Meli, A.; Vizza, F. *Organometallics* **1995**, *14*, 4858.

Scheme 43



Scheme 44



F. Dioxothiapentadienyl−Metal Complexes. Paz-Sandoval[49] has recently begun to investigate the reactivity of 5,5-dioxo-5-thiapentadienide (or "butadienesulfonyl anion"), $CH_2{=}CHCH{=}CHSO_2^-$, toward transition metals. This oxidized relative of thiapentadienide was first produced by Kloosterziel[39] via the base-induced electrocyclic opening of butadienesulfone, but Paz-Sandoval[50] has greatly expanded the scope of this synthetic approach.

As shown in Scheme 46, treatment of $(Cp^*IrCl_2)_2$ with the lithium salt of 5,5-dioxo-5-thiapentadienide or its 1,3-dimethylated analogue generated a novel dimer, **90**, which was held together by bridging lithium atoms. In each half of the dimer, the dioxothiapentadienyl ligand was bonded to the iridium center in an η^1 fashion through sulfur and was sickle-shaped with a cis internal double bond. When THF was removed from **90**, it immediately converted to the monomeric (1,2,5-η)-dioxothiapentadienyl complex **91**. When the *potassium* salt of 5,5-dioxo-5-thiapentadienide was used instead of the lithium salt, product **91** was generated directly (no dimeric intermediate was observed).

(48) Kawano, H.; Narimatsu, H.; Yamamoto, D.; Tanaka, K.; Hiraki, K.; Onishi, M. *Organometallics* **2002**, *21*, 5526.

V. Phosphapentadienyl-Metal Complexes

A. Phosphapentadienyl−Metal Complexes from Anionic Phosphapentadienide Reagents and Metal Halides. Our work in the area of phosphapentadienyl−metal complexes has involved the use of anionic phosphapentadienide reagents.[51] These reagents, though previously unknown, were readily synthesized by deprotonating the corresponding butadienylphosphines. Hence, lithium phosphapentadienide was produced by reacting butadienylphosphine with *n*-butyllithium, while lithium 2,4-dimethyl-5-phosphapentadienide was similarly synthesized from 1,3-dimethylbutadienylphosphine. The NMR spectra indicated that these anions were W-shaped in solution.

As shown in Scheme 47, treatment of $(Cl)Ir(PEt_3)_3$ with lithium phosphapentadienide led to the production of a phosphapentadienyl-bridged dimer, $[(\mu_2,\eta^1\text{-phosphapentadienyl})Ir(PEt_3)_2]_2$ (**92**). The NMR spectrum revealed the presence of two isomers, *trans* (**92a**) and *cis* (**92b**), in a ratio of 1.4:1.0. The structure of the *trans* isomer was determined by X-ray crystallography and showed the bridging phosphapentadienyl ligands to have W-shaped geometries. When crystals of *trans* isomer **92a** were redissolved, the 1.4:1.0 equilibrium mixture with the *cis* isomer was quickly reestablished. Double-labeling experiments proved that the *trans* → *cis* isomerization process did *not* involve the intermediacy of monomeric (phosphapentadienyl)$Ir(PEt_3)_2$ fragments.

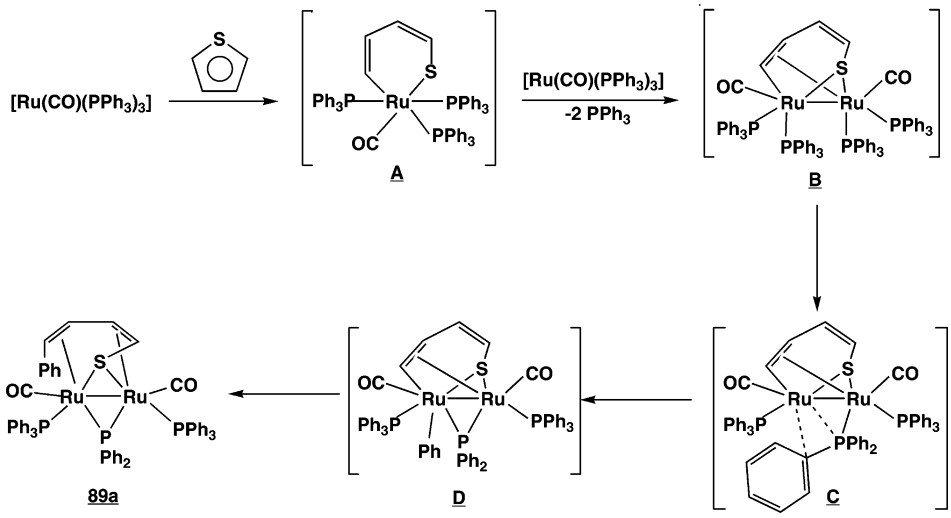
Similar results were observed in the reaction of $(Cl)Ir(PEt_3)_3$ with lithium 2,4-dimethyl-5-phosphapentadienide. Again, a phosphapentadienyl-bridged dimer was

(49) Gamero-Melo, P.; Cervantes-Vásquez, M.; Ramirez-Monroy, A.; Sánchez-Castro, M. E.; Paz-Sandoval, M. A. *Organometallics* **2004**, *23*, 3290.

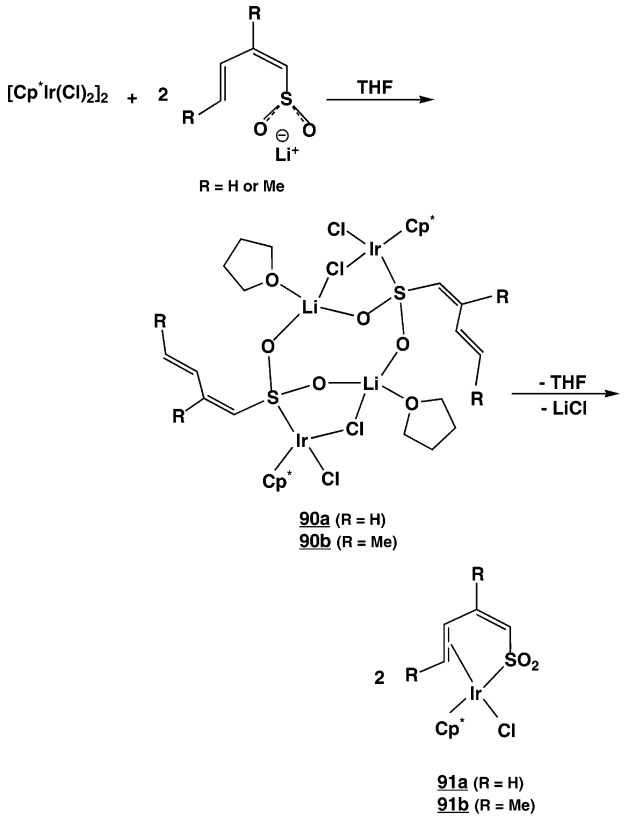
(50) Gamero-Melo, P.; Vallanueva-Garcia, M.; Robles, J.; Contreras, R.; Paz-Sandoval, M. A. *J. Organomet. Chem.* **2005**, *690*, 1379.

(51) (a) Bleeke, J. R.; Rohde, A. M.; Robinson, K. R. *Organometallics* **1994**, *13*, 402. (b) Bleeke, J. R.; Rohde, A. M.; Robinson, K. R. *Organometallics* **1995**, *14*, 1674.

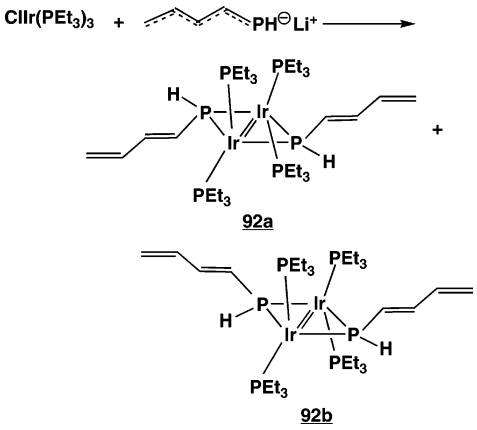
Scheme 45



Scheme 46



Scheme 47



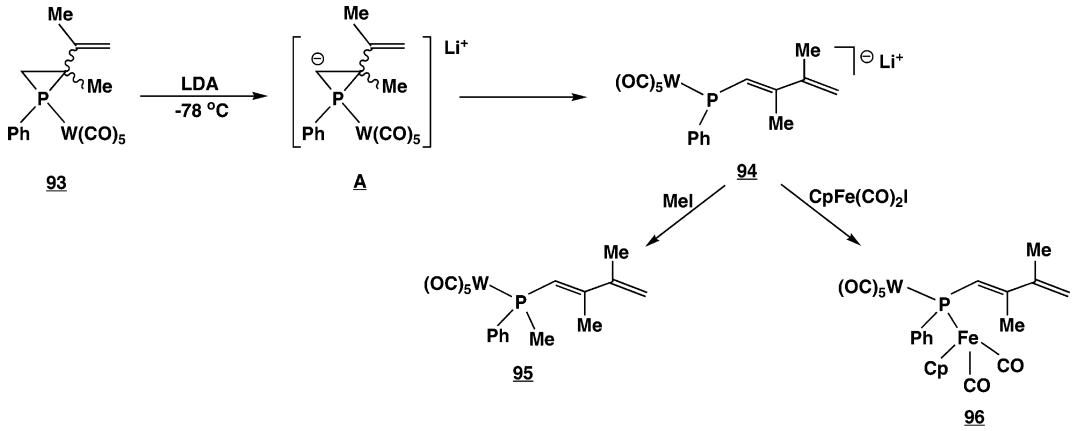
produced, but in this case the *trans* isomer was preferred by a ratio of 8:1 over the sterically encumbered *cis* isomer.

It is interesting to compare these (μ_2,η^1-phosphapentadienyl)Ir(PEt_3)$_2$ dimers with the (μ_2,η^1-thiapentadienyl)Rh(PEt_3)$_2$ dimer described earlier (cf. compound **79**; Scheme 39). While the chemical constituents of these compounds are very similar, their structures are different. In the phosphapentadienyl-containing compounds, the arrangement of the four phosphorus ligands around each iridium center is approximately tetrahedral, which allows for the formation of a strong iridium−iridium interaction (a double bond). In the thiapentadienyl compound, on the other hand, the coordination geometry around each rhodium center is square planar. This results in stable 16e rhodium centers with no metal−metal interaction.

B. Phosphapentadienyl−Metal Complexes from 2-Vinylphosphirane−Metal Precursors. A second synthetic approach to phosphapentadienyl−metal complexes, introduced by Mathey,[52] involved the conversion of a coordinated 2-vinylphosphirane ligand to a phosphapentadienyl ligand upon treatment with a bulky base. As shown in Scheme 48, the reaction of LDA with the 2-vinylphosphirane complex **93** (as a mixture of its two isomers) gave the corresponding phosphapentadienyl complex, **94**, as the lithium salt. This reaction involved abstraction of one of the CH_2 ring protons by LDA, followed by ring opening. Treatment of **94** with MeI or with $CpFe(CO)_2I$ *at room temperature* led to displacement of I^- by the nucleophilic phosphorus center, and the production of neutral derivatives **95** and **96**.

An X-ray crystal structure of the iron derivative **96** showed that the phosphapentadienyl ligand possessed a *trans* (*E*) geometry. However, when anion **94** was produced *at low temperature* (−78 °C) and then protonated at phosphorus before warming, both the *cis* (*Z*) and *trans* (*E*) isomers of the ligand were observed. This implied that the two isomers of precursor **93** gave rise to different isomers of **94** (*E* and *Z*) but that $Z \rightarrow E$ conversion occurred in the phosphapentadienyl ligand upon warming to room temperature.

Scheme 48



VI. Final Thoughts

While rational synthetic approaches have now been developed for all four classes of heteropentadienyl−transition-metal complexes (oxa-, aza-, thia-, and phosphapentadienyl), some synthetic limitations still remain and need to be addressed. For example, all of the azapentadienyl−metal complexes that have been synthesized to date possess bulky alkyl substituents on the nitrogen atom. The presence of this bulky group strongly influences the physical and chemical properties of the azapentadienyl−metal complexes.

The number and variety of bonding modes that heteropentadienyl ligands adopt are remarkable. In addition, facile interconversions between bonding modes can occur, and these lead to enhanced reactivity. For example, $\eta^5 \rightarrow \eta^3$ or $\eta^3 \rightarrow \eta^1$ shifts free up coordination sites at the metal center and allow ligand addition or oxidative addition reactions to proceed. While these kinds of ligand shifts are also observed in pentadienyl−metal chemistry, it appears that they are even more facile in heteropentadienyl−metal complexes, where the interaction between the C−X π-bond and the metal center is often relatively weak. The multitude of available bonding modes, coupled with the ease of shutttling between them, raises the exciting possibility of ultimately using heteropentadienyl−metal complexes in homogeneous catalysis.

Other applications of these complexes are already being pursued. For example, thiapentadienyl−metal complexes are excellent models for intermediates in hydrodesulfurization (HDS) reactions, and their chemistry can offer insights into the mechanism of this important industrial process.[38,44−48] In addition, thiapentadienyl−metal complexes offer enormous potential in the synthesis of unusual organosulfur compounds though electrophilic addition/ligand displacement sequences.[47] Oxapentadienyl− and thiapentadienyl−metal complexes are being employed as precursors to novel organometallic ring systems, including aromatic metallacycles such as metallafurans,[19e] metallapyryliums,[53] metallathiophenes,[41] and metallathiabenzenes.[54] Finally, η^3-oxapentadienyl−metal complexes are being utilized in the stereoselective functionalization of ketone groups.[13,16] These diverse applications point to the broad potential of hetereopentadienyl−metal complexes and give ample reason to believe that the future of this field is bright.

Note Added in Proof. Mindiola[55] has recently synthesized an azapentadienyl−Ti complex by an intramolecular Wittig-type reaction involving a titanium neopentylidene and the imine functionality of a Nacnac ligand.

OM058044+

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