Chemistry of η^2-Acyl, η^2-Iminoacyl, and Related Functional Groups

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Contents

I. Introduction

The migratory insertion of carbon monoxide into metal–alkyl and metal–hydride bonds is an extremely important organometallic reaction that has deservedly received considerable study by synthetic, mechanistic, and theoretical research groups.[1-7] Much of this work stems from the importance of carbonylation reactions (both stoichiometric and catalytic) in which the migratory insertion is the key step whereby the carbon monoxide is activated by the transition metal system.[8] However, it is the reactivity of the ensuing metal acyl or metal formyl that determines the types of organic products that one can obtain using carbon monoxide as a chemical feedstock.[8] One important characteristic of acyl functionalities is their observed ability, in some cases, to bind to the same metal through both the carbon and oxygen atoms (Scheme I).[9] This η^2-binding typically occurs around electron-deficient metal centers

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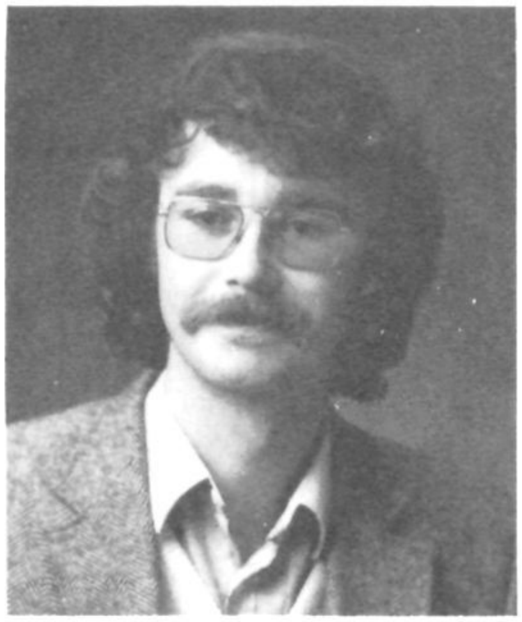

Ian Rothwell was born in Manchester, England, in 1955. After receiving his B.Sc. (1976) and Ph.D. (1979) from University College London under the supervision of A. J. Deeming, he moved to Indiana University to carry out postdoctoral research with Malcolm M. Chisholm. After an exciting and incredibly stimulating 2 years at Indiana University, he moved to Purdue University, where he is currently Associate Professor. A current recipient of an Alfred P. Sloan Fellowship and Camille and Henry Dreyfus Teacher–Scholar grant, Professor Rothwell's interests lie in the area of early transition metal inorganic and organometallic chemistry.

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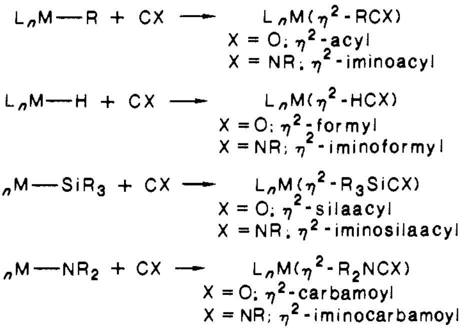
SCHEME I



and is particularly characteristic for acyls bound to high-valent, early d-block, lanthanide, and actinide metal centers. In these latter cases the coordination through oxygen results in reactivity significantly different from that of their η^1-bound counterparts. Also related to the carbonylation of metal–alkyl and metal–hydride bonds is the migratory insertion of CO into other metal–ligand bonds as well as reactions involving the insertion of other molecules such as alkyl isocyanides[10] and carbon monosulfide,[11] which are isoelectronic with CO. Again it is possible for the new groups generated by these reactions to adopt an η^2-bonding mode, and some of these are shown (Scheme I). Reactivity studies indicate that the chemistry of these related functionalities can complement that of the parent acyl or formyl and sometimes give insight into the importance of various steric and electronic effects on the reactivity of these η^2-bound groups.

The past 15 years has seen many developments in the chemistry of η^2-acyl and related functional groups. This paper is meant as a comprehensive review of this work, covering not only aspects of synthesis, structure, spectroscopy, and reactivity but also theoretical and mechanistic insights that have been reported.

II. Synthetic Strategies

A. Migratory Insertion of CO and RNC

The direct interaction of carbon monoxide (sometimes with pressure) or organic isocyanides with the transition metal substrate accounts for the majority of compounds that have been reported. Such migratory insertion reactions have been observed into metal–carbon, metal–hydrogen, metal–silicon, metal–nitrogen, and metal–phosphorus bonds, and they will be covered in this order.

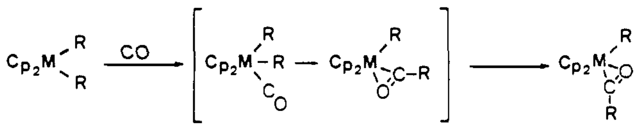
1. Into Metal–Alkyl Bonds

The migratory insertion of carbon monoxide or alkyl isocyanides in metal–alkyl bonds leading to η^2-acyl and η^2-iminoacyl functions has been observed for most of the early d-block metals as well as numerous actinide and lanthanide elements. The pioneering work (1974) by Floriani on the reaction of CO with $Cp_2Ti(R)Cl$[12] has been followed by many studies dealing with the carbonylation of group 4 metallocene substrates of the type $Cp_2M(R)X$ (X = alkyl, halide, alkoxide, etc.) (eq 1).

$$Cp_2M(R)X + CO \rightleftharpoons Cp_2M(\eta^2\text{-}RCO)X \qquad (1)$$
$$M = Ti, Zr, Hf$$

These 16-electron alkyls are found to reversibly absorb 1 equiv of CO to generate the 18-electron mono(η^2-acyls). The η^2-bonding is strongly indicated by spectroscopic properties and confirmed by structural studies (vide infra). The reversibility of the migratory insertion reaction is readily demonstrated, and thermodynamic data for the alkyl/acyl equilibrium have been obtained (section V.A). Work by Caulton et al. has indicated a strong dependence of the equilibrium on the ancillary ligand X in compounds of the type $Cp_2Zr(CH_3)X$.[13] The equilibrium constant for formation of the η^2-acyl was found to decrease as follows: $X = CH_3 > Cl > OEt$. This was argued to reflect increasing competition between the acyl oxygen and π-donating orbitals on X for the vacant orbital on the metal.

SCHEME II



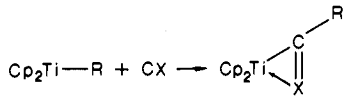
Theoretical studies of metallocene substrates of the type Cp_2MR_2 (M = Ti, Zr, Hf)[14] indicate that the only vacant orbital to which the incoming CO ligand can donate prior to insertion lies between the metallocene sandwich. A careful mechanistic study by Erker[15] on the carbonylation of $Cp_2Zr(CH_3)_2$ showed that the initially formed η^2-acyl product contained the oxygen atom outside or away from the noninserted alkyl bond. This kinetic product was then found to isomerize to the thermodynamically more stable O-inside isomer at −60 °C. This observation was interpreted as indicating that the CO molecule initially binds to the metal on the outside, instead of between the two alkyl groups (Scheme II). A series of low-temperature infrared experiments by Bercaw and Caulton have actually detected the carbon monoxide adduct of $Cp^*_2MH_2$ (M = Zr, Hf).[16] In this case the CO was found to coordinate between the two hydride ligands, and the reduction in $\bar{\nu}(CO)$ on coordination was attributed to back-donation of the hydride ligands into the π^*_{CO} orbital.[16] Similar carbonylation reactions are observed for the more bulky derivatives $Cp^*_2ZrR_2$.[17]

A number of competitive carbonylation reactions involving substrates of the type $Cp_2M(R)(R')$ have been reported. In an early study, Lappert showed that insertion of CO occurs into the most sterically hindered metal–alkyl bond of $Cp_2Zr(CH_3)[CH(SiMe_3)_2]$.[18] In the case of the substrate $Cp_2Ti(C_6F_5)(CH_3)$, CO was found to insert into the Ti–CH_3 bond, while cyclohexyl isocyanide was found to insert into the Ti–C_6F_6 bond[19] (eq 2).

$$Cp_2Ti(C_6F_5)(CH_3) + CO \rightarrow Cp_2Ti(\eta^2\text{-}CH_3CO)(C_6F_5)$$
$$Cp_2Ti(C_6F_5)(CH_3) + (cy)NC \rightarrow Cp_2Ti(\eta^2\text{-}(cy)NCC_6F_5)(CH_3) \qquad (2)$$
$$cy = c\text{-}C_6H_{12}$$

The reactivity of the group 4 metallocene alkyls with organic isocyanides has been less studied.[20] The resulting η^2-iminoacyls appear much more stable than their oxygen counterparts toward deinsertion, and to date there has been no report of the reversing of this reaction even under forcing conditions. Some representative reactions are shown (eq 3 and 4). Both N-in and N-out isomers have been characterized, and in at

SCHEME III



X = xy, R = Me, Et, Bu^n, Bu^s, Bu^t, η^3-allyl, Ph, *trans*-CMe=CHMe, η^3-(1-methylallyl)
X = O, R = *o*-tolyl, *trans*-CMe=CHMe

least one case the two forms have been shown to be in equilibrium.[21,22]

$$Cp_2Zr(Cl)CH(SiMe_3)_2 + (p\text{-tol})NC \rightarrow Cp_2Zr(Cl)[\eta^2\text{-}(p\text{-tol})NCCH(SiMe_3)_2] \quad (3)$$

$$p\text{-tol} = 4\text{-}MeC_6H_4$$

$$Cp_2Zr(OAr)CH_2Ph + Bu^tNC \rightarrow Cp_2Zr(OAr)(\eta^2\text{-}Bu^tNCCH_2Ph) \quad (4)$$

$$OAr = 2\text{-methyl-6-}tert\text{-butylphenoxide}$$

The reactivity of the related d^1-metal alkyls Cp_2TiR has been investigated by Teuben et al.[24-32] Insertion of CO and RNC yields η^2-bound functionalities as indicated by spectroscopic data (Scheme III). This η^2-bonding was confirmed structurally for $Cp_2Ti(\eta^2\text{-}PhCN\text{-}2,6\text{-}C_6H_3Me_2)$.[29] In the case of the 1-methylallyl compound insertion of xylyl isocyanide was found to take place at the unsubstituted end of the alkyl fragment.[26] The oxidation of many of these Ti(III) compounds with I_2 or PhSSPh results in Ti(IV) compounds in which the acyl or iminoacyl remains η^2-bound.[33]

Somewhat stoichiometrically related to the chemistry of the group 4 metallocene η^2-acyls are the extensive and thorough studies by Marks et al. on the carbonylation of the actinide alkyls of stoichiometry $Cp^*_2M(R)X$ (M = Th, U).[34,35] Facile, irreversible insertion of CO is found to produce a number of mono(η^2-acyls), which have been characterized both spectroscopically and, in a number of cases, structurally (Scheme IV).[36-38] Again both O-inside and O-outside isomers have been observed.

The carbonylation of a series of compounds Cp_3ThR has been studied kinetically (eq 5).[39] The rate of

$$Cp_3ThR + CO \xrightarrow{23\ °C} Cp_3Th(\eta^2\text{-}COR) \quad (5)$$

$$R = Pr^i,\ Bu^n,\ neo\text{-}C_5H_{11},\ Bu^s,\ Me\ (45\ °C)$$

formation of the resulting η^2-acyl was found to be first order in both the alkyl substrate and CO. In contrast to the irreversible carbonylation seen for $Cp^*_2M(R)X$ (M = Th, U), Zanella observed that decarbonylation of $Cp_3U(\eta^2\text{-}RCO)$ could be achieved at 60 °C.[40]

The insertion of alkyl isocyanides into the U–R bonds of $Cp^*_2U(R)X$ and Cp_3UR compounds has been investigated (eq 6 and 7).[41,42] Both yield stable η^2-iminoacyls that do not undergo deinsertion on thermolysis.

$$Cp_3UR + R'NC \rightarrow Cp_3U(\eta^2\text{-}R'NCR) \quad (6)$$

$$R = Bu^n;\ R' = Bu^t,\ c\text{-}C_6H_{11},\ 2,6\text{-dimethylphenyl}$$

$$R = CH_3;\ R' = c\text{-}C_6H_{11}$$

$$Cp^*_2U(X)R + Bu^tNC \rightarrow Cp^*_2U(X)(\eta^2\text{-}Bu^tNCR) \quad (7)$$

$$R = CH_3;\ X = CH_3,\ Cl$$

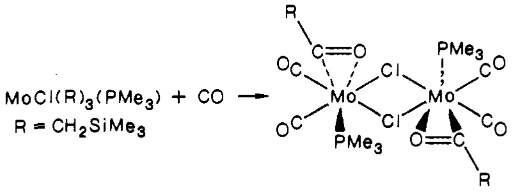
$$R = Bu^n;\ X = Cl$$

SCHEME IV

$$Cp^*_2Th(CH_2Bu^t)Cl + CO \rightarrow Cp^*_2Th(\eta^2\text{-}COCH_2Bu^t)Cl$$
O-outside

$$Cp^*_2Th(Ph)Cl + CO \rightarrow Cp^*_2Th(\eta^2\text{-}COPh)Cl$$
O-inside

SCHEME V



The lanthanide alkyl $Cp_2Lu(CMe_3)(thf)$ has been shown by Evans et al. to react rapidly with CO (1 equiv) to yield the corresponding η^2-acyl complex (eq 8).[43,44]

$$Cp_2Lu(CMe)_3(thf) + CO \rightarrow Cp_2Lu(\eta^2\text{-}COCMe_3) + thf \quad (8)$$

The number of stable, isolated η^2-acyl compounds that do not contain predominantly cyclopentadienyl type ligation are few. However, η^2-acyls are routinely proposed as the reactive intermediates formed during the carbonylation of a number of early transition metal alkyl compounds that leads to other products (section V). The Mo(IV) alkyl compound $MoCl(CH_2SiMe_3)_3(PMe_3)$ readily reacts with CO to produce a Mo(III) chloro-bridged dimer containing η^2-acyl groups bound to both metals (Scheme V).[45] The tungsten analogue has also been reported.[46] Somewhat related products resulted from attempts to alkylate the carbonyl halide $MoCl_2(CO)_2(PMe_3)_3$ with $Mg(CH_2SiMe_3)_2$.[47] The presumably intermediate monoalkyl $MoCl(CH_2SiMe_3)(CO)_2(PMe_3)_3$ rearranges to the finally observed η^2-acyl product.[47]

Curtis et al. have also generated a series of η^2-acyls of molybdenum by attempted alkylation of the carbonyl anions $TpMo(CO)_3^-$.[48,49] Treatment with MeI or Me_3O^+ leads to the compound $TpMo(CO)_2(\eta^2\text{-}COMe)$, again via an alkyl intermediate.

The tungsten carbyne compound $CpW(CO)_2(CR)$ (R = CH_3, *p*-tolyl) will react with 2 equiv of HCl.[50] However, no intermediate alkyl $CpW(CO)_2Cl_2(CH_2R)$ is seen, an η^2-acyl isomer being obtained. Somewhat related is the η^2-acyl complexes formed by ligand addition (L = CO, $P(OMe)_3$, PMe_3) to $CpW(CO)(C_2H_2)(CH_3)$ (eq 9).[51]

$$CpW(CO)(C_2H_2)CH_3 + L \rightarrow CpW(\eta^2\text{-}COCH_3)(L)(C_2H_2) \quad (9)$$

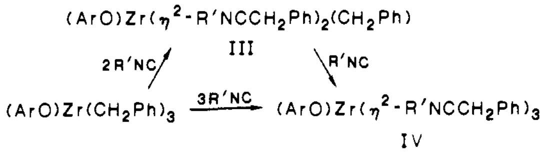
In the case of η^2-iminoacyls, many more stable examples are now known than their oxygen counterparts, especially where supported by non-Cp based ligation. Furthermore, there are also examples of complexes containing more than one η^2-iminoacyl bound to the same metal center, a situation as yet unknown for η^2-acyl ligands. Treatment of a series of mixed alkyl,aryl oxides of the group 4 and group 5 metals with various alkyl isocyanides has led to the isolation and characterization of a large number of η^2-iminoacyl derivatives containing aryl oxide coligation (Schemes VI–VIII).[20] Ine one case a total of three, equally η^2-bound iminoacyls were shown to be attached to a single

SCHEME VI

$$(ArO)_2M(R)_2 \xrightarrow{R'NC} \underset{I}{(ArO)_2M(\eta^2\text{-}R'NCR)(R)} \xrightarrow{R'NC} \underset{II}{(ArO)_2M(\eta^2\text{-}R'NCR)_2}$$

compd	M	ArO	R	R′
Ia	Ti	OAr-2,6-Pr^i_2	CH_2Ph	Bu^t
Ib	Ti	OAr-2,6-Ph_2	CH_2SiMe_3	Ph
Ic	Ti	OAr-2,6-Ph_2	CH_2SiMe_3	xy
Id	Ti	OAr-2,6-Ph_2	CH_2Ph	xy
Ie	Zr	OAr-2,6-Bu^t_2	CH_2Ph	xy
IIa	Ti	OAr-2,6-Pr^i_2	CH_2Ph	xy
IIb	Ti	OAr-2,6-Ph_2	CH_2Pr	xy
IIc	Zr	OAr-2,6-Bu^t_2	CH_2Ph	xy
IId	Zr	OAr-2,6-Bu^t_2	CH_2Ph	Bu^t
IIe	Zr	OAr-2,6-Bu^t_2	CH_3	xy
IIf	Zr	OAr-2,6-Bu^t_2	CH_3	Ph
IIg	Hf	OAr-2,6-Bu^t_2	CH_3	Ph

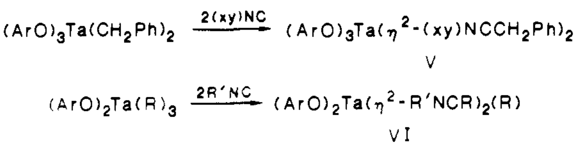
SCHEME VII



ArO = OAr-2,6-Bu^t_2

III, R′ = xy; IVa, R′ = Bu^t; IVb, R′ = xy

SCHEME VIII



ArO = OAr-2,6-Me_2

VIa, R = CH_3, R′ = xy; VIb, R = CH_3, R′ = iso

VIc, R = CH_2Ph, R′ = xy; VId, R = CH_2Ph, R′ = iso

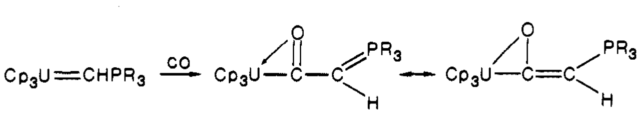
Zr(IV) metal center in $Zr(\eta^2\text{-}Bu^tNCCH_2Ph)_3(OAr)$ (OAr = 2,6-di-*tert*-butylphenoxide).[20] All of the reactions proceed in excellent yield and some synthetic control of the amount of insertion is typically present, allowing the isolation of compounds containing different η^2-iminoacyl groups. For the tantalum trialkyl $Ta(OAr)_2R_3$ (R = CH_3, CH_2Ph, Ph) insertion into only two of the metal–alkyl bonds with aryl isocyanides was found possible, leading to a bis(η^2-iminoacyl) derivative (Scheme VIII).[20,52] This result is reminiscent of the early work of Wilkins (1979), in which it was reported that $TaCl_2Me_3$ would insert only 2 equiv of cyclohexyl or *p*-tolyl isocyanide.[53] Interestingly, although the triphenyl $Ta(OAr)_2Ph_3$ will also react with only 2 equiv of Bu^tNC, the product is a mixed η^2-iminoacyl η^2-imine, the latter group formed by a double phenyl to Bu^tNC migration presumably through an intermediate bis(η^2-iminoacyl) alkyl (eq 10).[54]

$$Ta(OAr)_2Ph_3 + 2Bu^tNC \rightarrow Ta(OAr)_2(\eta^2\text{-}Bu^tNCPh_2)(\eta^2\text{-}Bu^tNCPh) \quad (10)$$

OAr = 2,6-dimethylphenoxide

Andersen et al. have shown that the group 4 alkyls $R_2M[N(CH_2SiMe_3)_2]$ (M = Zr, Hf) will react readily with Bu^tNC to produce bis(η^2-iminoacyl) compounds.[55] In contrast CO_2 is found to insert into the bulky metal–amido bond.[55]

SCHEME IX



The tris(pyrazolyl)borate compound $TpZr(OBu^t)Me_2$ has been shown to insert 1 equiv of Bu^tNC to produce a mono(η^2-iminoacyl) derivative.[56]

Treatment of the mixed carbonyl,isocyanide anion $CpMo(CO)_2(CNR)^-$ with MeI leads to an η^2-iminoacyl complex,[57,58] while $CpTa(\eta^2\text{-}ArCCAr)(CH_3)_2$ (Ar = phenyl, *p*-tolyl) will insert 1 equiv of Bu^tNC to yield a mixed η^2-iminoacyl,η^2-acetylene compound.[59]

Several low-valent vanadium complexes have been reported.[60,61] The room temperature reaction of CO (1 atm) with Cp_2VR (R = Me, Ph) yields green-maroon crystals of the desired η^2-acyl complexes.[60] In the R = Ph reaction, a competing ligand-induced aryl migration to a Cp ring was found. Franke and Weiss observed that treatment of $[Et_4N][V(CO)_4L_2]$ salts (L_2 = diphos, arphos) with triphenylcyclopropenylium bromide under photolytic conditions gives $V(CO)_3L_2(\eta^2\text{-}COC_3Ph_3H_2)$.[42]

In bimetallic systems, $Cp_2Zr(CH_3)[(CO)_3MCp]$ (M = Cr, Mo, W) readily undergo carbon monoxide insertion to give $Cp_2Zr(\eta^2\text{-}COMe)[(CO)_3MCp]$ products.[62–64] The related titanium compounds, $Cp^*_2Ti(\eta^2\text{-}COR)[(CO)_3MoCp]$ (R = Me, *neo*-C_5H_{11}), have been isolated via the reaction of $Cp^*_2Ti(\eta^2\text{-}COR)$ and $[CpMo(CO)_3]_2$.[65] In an early transition metal, main group metal bimetallic system, the species $Cp_2Ti(\eta^2\text{-}COMe)(GePh_3)$ was recently isolated and characterized.[66]

There is one migratory insertion reaction that does not give a "strict" η_2-acyl complex. Cramer et al. reported that CO reacts with $Cp_3U{=}CHPR_3$ to give the new compound $Cp_3U[(OCCH)PR_3]$ (Scheme IX).[67a] Structural data show that resonance form B contributes significantly to the electronic character of this molecule. A similar reaction between $Cp_2U{=}CHPPh_2Me$ and (cy)NC yields a related η^2-iminoacyl.[67b]

In a series of pioneering studies, Roper et al. isolated and structurally characterized a series of η^2-acyl, η^2-iminoacyl, and η^2-thioacyl derivatives of Ru and Os.[68] The method of preparation involved a migratory insertion rearrangement reaction involving 18-electron alkyl precursors. Hence the Ru(II) methyl compound $RuCH_3(I)(CO)_2(PPh_3)_2$ rearranges to the η^2-acyl $Ru(\eta^2\text{-}COCH_3)(I)(CO)(PPh_3)_2$.[68a] The mixed carbonyl,isocyanide complex Ru(*p*-tolyl)Cl(CO)(CNR)$(PPh_3)_2$ was found to generate an η^2-iminoacyl derivative,[68b] while η^2-thioacyl products were preferentially formed from Os(*p*-tolyl)(X)(CS)(CO)$(PPh_3)_2$ or Os(*p*-tolyl)(X)(CS)(CNR)$(PPh_3)_2$ (X = halide).[68c] Much more recently, Roper et al. reported the synthesis of isoelectronic methylene,η^2-acyl compounds: $M(\eta^2\text{-}COR)(CH_2)(Cl)(PPh_3)_2$ (M = Ru, Os; R = Ph, *o*-tolyl, *p*-tolyl).[68d] The synthesis was achieved by treating $M(R)Cl(CO)(PPh_3)_2$ fragments with diazomethane, the intermediate alkyl,carbonyl compounds being in equilibrium with the η^2-acyl derivatives.[68d]

Recent work by Hoffman et al. has shown that carbonylation of the oxo,alkyl $ReO(PMe_3)(CH_2SiMe_3)_3$ yields a purple η^2-acyl.[69a] In an interesting study Girolami has shown that carbonylation of the iron neopentyl compound $Fe(CH_2CMe_3)X$(dippe) (dippe =

$Pr^i{}_2PCH_2CH_2PPr^i{}_2$) leads initially to an η^2-acyl, $Fe(\eta^2\text{-}COCH_2CM_3)X(CO)(dippe)$, which then reacts with a further equivalent of CO to produce the η^1-acyl, $Fe(\eta^1\text{-}COCH_2CMe_3)(X)(CO)_2(dippe)$.[69b] The use of the more bulky aryl substituent mes = 2,4,6-trimethylphenyl in Fe(mes)(Br)(dippe) resulted in the formation of only the η^2-acyl compound $Fe(\eta^2\text{-}CO(mes))Br(CO)(dippe)$.[69b]

The oxidative addition of Pr^iI to $Fe(CO)_2L_2$ fragments (L = PEt_3, $P(OMe)_3$) has also been shown to yield the η^2-acyl compound $Fe(\eta^2\text{-}COPr^i)I(CO)(L)_2$.[69c]

2. *Into Metal–Hydride Bonds*

The migratory insertion of carbon monoxide into a metal–hydride bond to produce a metal–formyl moiety has been discussed as a primary event in a number of metal-mediated catalytic and stoichiometric hydrogenations of CO.[8] The thermodynamic and kinetic aspects of this reaction compared to those of the analogous insertion into metal–alkyl bonds have been discussed widely.[70] There are many reactions of early transition metal hydride reagents with CO that lead to products containing organic fragments resulting from carbonyl reduction. However, in most of these reactions, detection of the proposed intermediate metal η^2-formyls was found impossible. In some cases the use of organic isocyanides has allowed the characterization of isoelectronic η^2-iminoformyl functions. Hence although reaction of $Cp^*{}_2ZrH_2$ with CO leads to products derived from an undetected intermediate η^2-formyl,[71a] the use of RNC (R = CH_3, 2,6-dimethylphenyl) by Bercaw and Wolczanski allowed the isolation of compounds of the type $Cp^*{}_2Zr(H)(\eta^2\text{-}HCNR)$.[71b]

The organoactinide reagents $(Cp^*{}_2ThH_2)_2$ developed by Marks et al. similarly show a high potency for reduction of CO.[34,35,37,72] The alkoxide compounds $Cp^*{}_2Th(H)(OR)$ were found to reversibly and rapidly insert 1 equiv of CO to generate stable, spectroscopically characterized η^2-formyls (eq 11).[37]

$$Cp^*{}_2Th(H)(OR) + CO \rightleftarrows Cp^*{}_2Th(\eta^2\text{-}COH)(OR) \quad (11)$$

$$R = CHBu^t{}_2;\ 2,6\text{-di-}tert\text{-butylphenyl}$$

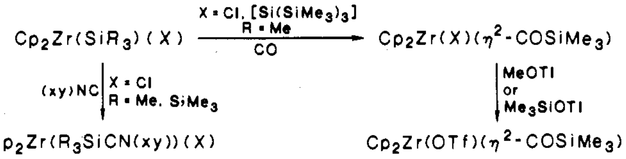
Kinetic studies showed the reaction to be first order in both metal hydride and CO and to demonstrate a primary kinetic isotope effect, $k_H/k_D = 2.8\ (4)$ at -54 °C. It was also determined that the rate of hydride migration greatly exceeded that of alkyl migration in related compounds.[37] Three other examples of early transition metal η^2-formyls include $Cp^*{}_2V(CHO)(CO)$,[73] $Ta_2(Cp^*Et)_2Cl_5(CHO)$,[74] and $Ta_2(Cp^*Et)_2Cl_4H(CHO)$.[74] In the latter case, the η^2-formyl is actually "side-on" bridging.

Evans has characterized μ,η^2-*N*-alkylformimidoyl complexes of erbium and yttrium, $[(C_6H_4R)_2Ln(\mu,\eta^2\text{-}HCNBu^t)]_2$ (Ln = Er, Y; R = H, Me)[76,77] formed by the addition of Bu^tNC to the corresponding hydride.

3. *Into Metal–Silicon Bonds*

Recent work by Tilley et al. has dramatically extended the known chemistry of the transition metal–silicon bond.[78,79] Using substrates of the type $Cp_2Zr(SiR_3)(X)$ he has shown that both η^2-silaacyls and η^2-silaiminoacyl products can be obtained by interaction with CO and RNC molecules (Scheme X). The compound $Cp_2Zr(SiMe_3)(Cl)$ reacts reversibly with CO, giving the η^2-acyl complex under pressure (50–100 psi), and thermally undergoes deinsertion under 1 atm of N_2. A competitive reaction using $Cp_2Zr(CH_3)[Si(SiMe_3)_3]$ leads only to the metal η^2-acyl. In contrast to the zirconocene system, $Cp_2Ti(SiMe_3)(Cl)$ undergoes igand-induced reductive elimination of Me_3SiCl on treatment with CO.[78]

SCHEME X



4. *Into Metal–Amido Bonds*

The reaction of transition metal amides with CO has been less extensively studied than their reactions with CO_2.[80] In 1981 Marks et al. reported the facile insertion of CO into actinide metal–dialkylamide bonds.[81] The substrates $Cp^*{}_2M(NR_2)Cl$ and $Cp^*{}_2M(NR_2)_2$ (M = Th, U) were found to yield the corresponding η^2-carbamoyl products. Interestingly, insertion into both metal–amido bonds was found possible, leading to a bis(η^2-carbamoyl) product (eq 12). A competitive experiment using $Cp^*{}_2Th(NMe_2)(Me)$ showed that insertion occurred into the metal–alkyl bond.[81]

$$Cp^*{}_2M(NR_2)_2 + 2CO \rightarrow Cp^*{}_2M(\eta^2\text{-}CONR_2)_2 \quad (12)$$

$$M = Th,\ R = CH_3;\ M = U,\ R = CH_3,\ C_2H_5$$

More recent studies have shown that the insertion of organic isocyanides into the $U\text{-}NR_2$ bonds of $Cp^*{}_2U(NEt_2)(X)$ is possible to produce η^2-iminocarbamoyl ligands.[82] Again the metal–alkyl bond in the compound $Cp^*{}_2U(NEt_2)(Me)$ was shown to undergo preferential insertion to generate an η^2-iminoacyl (eq 13). Although there were initial reports that Cp_3UNEt_2 was unreactive to RNC molecules, Zanella et al. found that insertion in fact can take place.[83]

$$Cp^*{}_2U(NEt_2)(CH_3) + RNC \rightarrow Cp^*{}_2U(NEt_2)(\eta^2\text{-}COCH_3) \quad (13)$$

Chisholm et al. have shown that the extremely air- and moisture-sensitive compound $Mo(NMe_2)_4$ can undergo a range of different reactions with a variety of small molecules. With CO, a trinuclear product is produced containing three different types of carbamoyl ligand, one of which is η^2-bound to one metal.[84] With 2,6-dimethylphenyl isocyanide, insertion into all four $Mo\text{-}NMe_2$ bonds takes place to produce a mononuclear product containing four η^2-carbamoyl groups (eq 14).[85]

$$Mo(NMe_2)_4 + 4(xy)NC \rightarrow Mo(\eta^2\text{-}(xy)NCNME_2)_4 \quad (14)$$

$$xy = 2,6\text{-dimethylphenyl}$$

5. *Into Metal–Phosphido Bonds*

The hafnium phosphido complex $Cp^*HfCl_2(PBu^t{}_2)$ has been shown to react with 1 equiv of CO at 25 °C to generate the η^2-carboxyphosphide product (eq 15).[86]

Zanella has also shown that η^2-(iminoalkyl)phosphide groups are generated by reaction of 2,6-dimethylphenyl isocyanide with $Cp_3U(PPh_2)$.[87]

$$Cp^*HfCl_2(PBu^t_2) + CO \rightarrow Cp^*HfCl_2(\eta^2\text{-}COPBu^t_2) \quad (15)$$

B. Miscellaneous Synthetic Methods

There are several miscellaneous reactions that result in the formation of η^2-acyl or η^2-iminoacyl complexes. One early method involved the oxidative addition of acyl halides to low-valent metal complexes. Floriani et al. have demonstrated that $Cp_2Ti(CO)_2$ and acyl halides (RCOX) (X = I, R = Me, Et, Pr^i, Bu^s; X = Cl, R = Me, Ph) react to give η^2-acyl complexes.[88] A whole series of vanadium η^2-acyl compounds have also been prepared by a similar procedure.[89]

An anomalous reaction of arenediazonium and diaryliodoso cations with $[Mo(CO)_3(Tp^*)]^-$ has been reported by Desmond et al.[90] The expected neutral CO displacement products were not obtained; instead the neutral η^2-aroyl complexes $Tp^*Mo(\eta^2\text{-}COAr)(CO)_2$ were observed. The process is believed to follow a free radical mechanism. Supporting this idea is the formation of cyclohexyl complexes, presumably via radical hydrogen abstraction from cyclohexane solvent.[90]

The reaction of vanadocene with the nitrilium salts $[PhC{\equiv}NMe]BF_4$ and $[MeC{\equiv}NMe]BF_4$ gives cationic η^2-iminoacyl complexes.[91] The paramagnetic products $Cp_2V(\eta^2\text{-}RC{=}NMe)BF_4$ are formed readily in tetrahydrofuran–acetonitrile mixtures.

III. Solid-State Structures

Solid-state structural studies have been performed on a variety of compounds containing one or more η^2-acyl or η^2-iminoacyl functions. Tables I and II present structural data for the η^2-acyl/η^2-iminoacyl portion of these molecules. Although a complete analysis of each structure cannot be given here, a summary of basic trends and general types of structures will be presented.

A. General Trends

The observed reactivity of the high-valent early transition metal η^2-acyl and related functionalities (section V) has led people to scrutinize the solid-state structures of compounds containing these ligands to try to gain some insight into the origin of this reactivity. As an example, early work focused on the possibility that ligands of this type could best be represented as metal-bound oxycarbenes or amidocarbenes.[17,34,35,70]

Analysis of the data presented in Tables I and II shows in nearly all cases that the values of the C–O and C–N distances are significantly shorter than expected for single bonds, lying in the 1.15–1.30-Å range for η^2-CO-containing compounds and an even narrower range of 1.24–1.29 Å for η^2-CN-containing compounds. This is consistent with the presence of double bonds.[92] In those cases where this parameter is larger, there are carbon substituents able to conjugate, e.g., NR_2, or else the unit is bridging two metal centers. The values of the M–C(η^2-acyl or η^2-iminoacyl) distances are similar to those found to alkyl groups bound to similar metal centers.[93] In the case of the M–O(η^2-acyl) or M–N-(η^2-iminoacyl) distances, the values appear to be somewhat shorter than found for oxygen-bound (e.g., ethers) and nitrogen-bound (e.g., pyridines) neutral donors but longer than expected for metal–alkoxy or metal–amido bonds.[94] Hence, the structural parameters indicate a stronger interaction with the heteroatom than one would predict based on a simple η^2-acyl or η^2-iminoacyl picture, but not quite as strong as would be expected for an oxy–carbene or amido–carbene resonance. Recent theoretical work has indicated that the reactivity and electronic structure of these η^2-groups can also be accommodated into alternate charged resonance forms (section V).

In the case of η^2-acyls, considerable interest has focused on a parameter Δ, defined as $\Delta = d(\text{M–O}) - d(\text{M–C})$. Attempts have been made to correlate this parameter with d(C–O) and ν(CO) in order to show the importance as well as contribution of the oxy–carbene resonance.[48] Table I lists this parameter, and the compounds are listed in order of decreasing values of Δ. Curtis et al. has reported little correlation between Δ and d(C–O) or ν(C–O).[48] In some cases a correlation of Δ can be made with the oxophilicity of the metal as measured by the heats of formation of the binary metal oxides.[36,69b,95,96]

There is a definite correlation between the value of Δ and the electron deficiency of the metal center. This is clearly seen in Table Ia, where the use of this parameter splits the reported η^2-acyls into two distinct groups. The first, containing lower valent metals, has the largest values of Δ, while the second, containing high-valent (d^0) metal centers, has the lowest values of Δ. Even smaller values of Δ are seen to occur for η^2-carbamoyl (η^2-$OCNR_2$) groups. However, here conjugation with the NR_2 substituent probably leads to lengthening of the M–C bond.

Structural parameters for η^2-iminoacyls collected in Table II show a much smaller variation in the values of d(M–N) − d(M–C).[20] However, the correlation with electron deficiency of the metal center is evident as with the η^2-acyls.

With these general patterns in mind, we will discuss specific structural examples. As with η^2-olefin complexes, it tends to be advantageous to consider η^2-acyl or η^2-iminoacyl ligands as occupying a single coordination site located midway along the CN bond. Isomers generated by orientations about this midpoint as well as facile rotation have been observed. However, in the case of fluxionality involving overall rotation, it is not known whether this actually takes place by rotation while η^2-bound (as with olefins) or by η^2–η^1–(rotation)–η^2 interconversions.

B. Metal Complexes

1. Group 4 Metal Complexes

There are a wide variety of group 4 metal compounds containing just one η^2-acyl or η^2-iminoacyl moiety. Two of the major stoichiometries are $Cp_2M(\eta^2\text{-}RCX)$[29] and $Cp_2M(\eta^2\text{-}RCX)(Y)$[12,63,66,79,88] molecules where X = O or NR′ and Y is an anionic ligand. Two typical examples are $Cp_2Ti((xy)NCPh)$[29] and $Cp_2Zr(COSiMe_3)(Cl)$.[79] These structures illustrate the typical metallocene "bent sandwich" configuration, with the planar η^2-moiety lying in an "equatorial girdle" around the metal center.

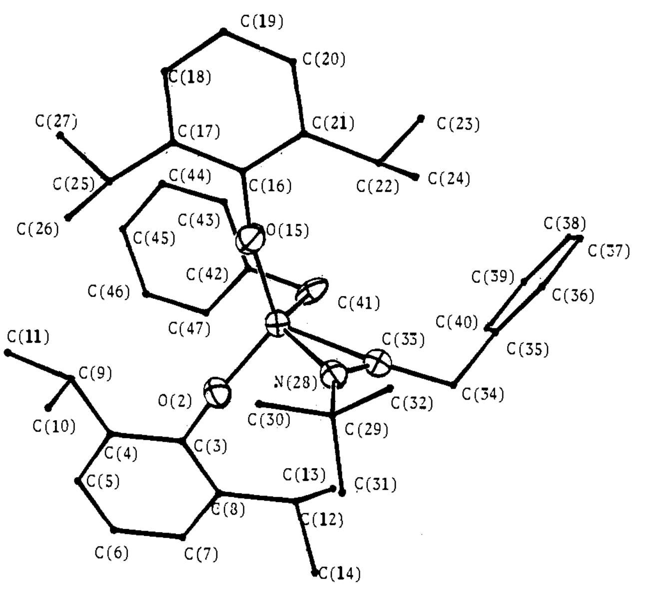
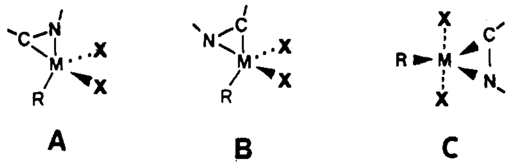


Figure 1. ORTEP view of Ti(OAr-2,6-Pr$^i_2$)$_2$(η^2-Bu^{t}NCCH$_2$Ph)(CH$_2$Ph) (OAr-2,6-Pr$^i_2$ = 2,6-diisopropyl phenoxide).

SCHEME XI



Typical Cp–M–Cp angles are 130–135°. The pseudotetrahedral molecules Cp$_2$M(η^2-RCX)(Y) can adopt one of two orientational possibilities for the η^2-ligand. Two ground-state structures can be envisioned, one (A) with the C→X vector toward (proximal to) the remaining Y ligand and the other (B) with the C→X vector away from (distal to) the remaining Y ligand (Scheme XI). In spectroscopic studies, Erker has shown that the kinetic product is B, while the thermodynamic product is A for Cp$_2$Zr(η^2-MeCO)(Me).[15]

Some related η^2-iminoacyl compounds of general formula (ArO)$_2$Ti(η^2-RCNR′)(R) have also been structurally characterized.[20] An ORTEP view of one of these molecules is shown in Figure 1. These pseudotetrahedral molecules do not have the electronic restrictions that the 18-electron metallocene derivatives do.[20] Hence, not only the proximal (A) and distal (B) isomers are viable ground-state structures, but also an alternate geometry C (Scheme XI) must be considered along with all conformers in between these idealized structures. As can be seen from Figure 2, the η^2-iminoacyl groups in these molecules adopt the distal orientation (B).

Two other compounds of L$_2$M(η^2-RCX)(Y) stoichiometry that should be mentioned are Cp$_2$Zr(η^2-COMe)(CO)$_3$MoCp[63] and Cl$_2$Hf(Cp′)(η^2-COPBu$^t_2$).[86] The former is noteworthy in that it can be regarded as an intimate ion pair consisting of [Cp$_2$Zr(η^2-COMe)]$^+$ and [(CO)$_3$MoCp]$^-$ ions. From the zirconium perspective, the CpMo(CO)$_3$ unit occupies a fourth coordination site via a bridging carbonyl, thus acting as Y in the stoichiometrical formula. The latter complex is unique in that it is the first carboxyphosphide derivative of a transition element. The phosphorus substituent on the acyl carbon results in a slight lengthening of the C–O distance [1.284 (6) Å] and a slight shortening of the P–C bond distance [1.782 (5) Å] (Table I). This, combined with spectroscopic data, suggests a π-bonding interaction between the acyl carbon and phosphorus atoms. As discussed earlier, η^2-carboxyamide structures also exhibit these features.

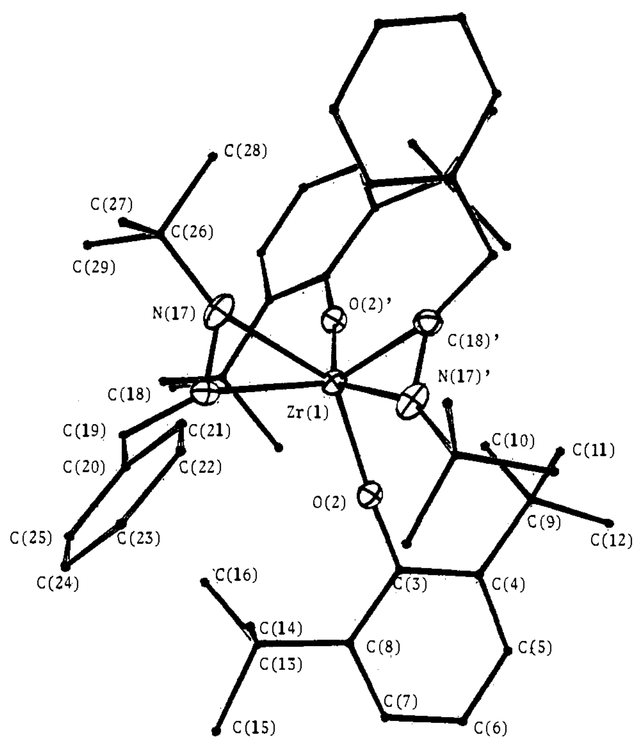
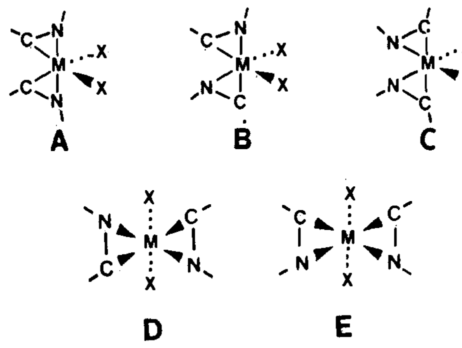


Figure 2. ORTEP view of Zr(OAr-2,6-Bu$^t_2$)$_2$(η^2-Bu^{t}NCCH$_2$Ph)$_2$.

SCHEME XII



As might be expected, a quite different structure is found for the stoichiometrically unrelated zirconium η^2-iminoacyl complex Tp*Zr(OBu^t)(η^2-MeCNBu^t)(Me).[56] The overall geometry is best described as a distorted octahedron with the η^2-iminoacyl ligand occupying a single coordination site.

There are two structurally characterized group 4 metal complexes that contain two η^2-iminoacyl ligands, M(OAr-2,6-Bu$^t_2$)$_2$(RCNR′)$_2$ (M = Hf, R = Me, R′ = Ph; M = Zr, R = CH$_2$Ph, R′ = Bu^t).[20] In contrast, there are no group 4 metal complexes known that contain two η^2-acyl ligands bound to the same metal center. The structure of the Zr bis(η^2-iminoacyl) is shown in Figure 2. There are a total of five possible idealized ground-state structures for molecules of stoichiometry X$_2$M(η^2-RCNR′)$_2$ (Scheme XII). A uranium complex is known that falls into category A. However, these two complexes (Zr and Hf) are significantly different and are more consistent with conformer D. Although formally six-coordinate, the molecules are again best described as pseudotetrahedral about the metal atom with

TABLE I. Structural Data for η^2-Acyl, η^2-Silaacyl, and η^2-Carbamoyl Complexes

compound	M—C=O, Å	M—O=C, Å	C=O, Å	d(M—O) − d(M—C), Å	∠M—C=O, deg	ref
Section a						
$Ru(COMe)I(CO)(PPh_3)_2$	1.88 (3)	2.47 (2)	1.33 (4)	0.59		*a*
$Os(CO\text{-}o\text{-}tol)Cl(CH_2)(PPh_3)_2$	1.86 (1)	2.423 (9)	1.22 (1)	0.56		*b*
$Ru(CO\text{-}p\text{-}tol)I(CO)(PPh_3)_2$	1.92 (1)	2.36 (1)	1.21 (2)	0.44		*a*
$Fe(CO\text{-}Pr^i)I(CO)(PEt_3)_2$	1.80 (2)	2.19 (2)	1.24 (2)	0.39		*c*
$Fe(CO\text{-}mes)Br(CO)(dippe)$	1.85 (1)	1.99 (1)	1.28 (2)	0.14		*d*
$[Mo(COC_6H_{11})(CO)_2\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]$	1.996 (9)	2.291 (6)	1.267 (11)	0.30		*e*
$MoCl(COCH_2SiMe_3)(CO)(PMe_3)_3$	2.024 (6)	2.324 (4)	1.234 (6)	0.30	87.5	*f*
$Mo(COPh)(CO)_2\{HB(3,5\text{-}Me_2C_3HN_2)_3\}$	2.005 (2)	2.287 (2)	1.245 (3)	0.28		*e*
$[MoCl(COCH_2SiMe_3)(CO)_2(PMe_3)]_2$	2.023 (3)	2.292 (2)	1.225 (4)	0.27	86.1 (2)	*g*
$[WCl(COCH_2SiMe_3)(CO)_2(PMe_3)]_2$	2.029 (7)	2.289 (5)	1.233 (9)	0.26	85.4 (5)	*f*
$TpMo(COMe)(CO)(PEt_3)$	2.002 (8)	2.246 (5)	1.279 (9)	0.25		*h*
$V(CO)_3(arphos)(COC_3Ph_3H_2)$	2.014 (14)	2.243 (11)	1.195 (18)	0.23	84.6 (7)	*i*
$TpMo(COMe)(CO)[P(OMe)_3]$	2.003 (6)	2.200 (4)	1.224 (8)	0.20		*h*
$TpMo(COMe)(CO)_2$	2.022 (9)	2.224 (6)	1.225 (11)	0.20		*j*
$[W(Cp)(Cl)_2(CO)(COCH_2CH_3)]$	1.999 (8)	2.167 (6)	1.246 (9)	0.17	80.2 (5)	*k*
$TpMo(COPh)(CO)_2$	2.021 (5)	2.189 (3)	1.224 (6)	0.17		*j*
$Cp_2Ti(COMe)Cl$	2.071 (2)	2.194 (14)	1.18 (2)	0.12	79.7 (6)	*l*
$Cp_2Zr(COMe)(Me)$	2.197 (6)	2.290 (4)	1.211 (8)	0.093	78.6 (4)	*m*
$Cp_2Ti(COMe)(GePh_3)$	2.15 (2)	2.220 (9)	1.15 (2)	0.07	78.1 (2)	*n*
$Cp_2Zr(COSiMe_3)(Cl)$	2.183 (2)	2.248 (1)	1.244 (3)	0.065	76.55 (13)	*o*
$Cp_2Zr(COMe)(CO)_3MoCp$	2.186 (4)	2.249 (3)	1.241 (5)	0.063	71.0 (2)	*p*
$Cp^*{}_2Th(COCH_2Bu^t)(Cl)$	2.44 (2)	2.37 (2)	1.18 (3)	−0.07	73 (1)	*q*
Section b						
$[Mo(NO)(OCNMe_2)(NCS)_4][PPh_4]_2$	2.029	2.078	1.322 (7)	0.05		*r*
$Cp^*{}_2Th(CONEt_2)(Cl)$	2.418 (20)	2.460 (16)	1.44 (3)	0.042	74.5 (11)	*s*
		2.383 (31)	1.53 (4)	−0.035	70.1 (15)	
$Cp^*{}_2U(CONMe_2)_2$	2.405 (8)	2.370 (5)	1.273 (10)	−0.035	73.0 (4)	*s*
	2.402 (9)	2.342 (7)	1.276 (12)	−0.058	71.8 (5)	
Section c						
$Cp^*HfCl_2(COPBu^t{}_2)$	2.203 (5)	2.117 (4)	1.284 (6)	−0.086	69.1 (3)	*t*
$Cp_3U[(OCCH)P(CH_3)(Ph)_2]$	2.37 (2)	2.27 (1)	1.27 (3)	−0.10	69 (1)	*u*
Section d						
$[(CpEt)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHO)$	2.085 (12)	2.094 (8)	1.496 (14)	~0 (av)		*v*
	2.119 (11)	2.089 (9)				

[a] Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46. [b] Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Shepard, W. E. B.; Wright, L. J. *J. Chem. Soc., Chem. Commun.* **1987**, 563. [c] Birk, R.; Berke, H.; Holtner, G.; Zsolnai, L. *J. Organomet. Chem.* **1986**, *309*, C18. [d] Hermes, A. R.; Girolami, G. S. *Organometallics* **1988**, *7*, 394. [e] Desmond, T.; Lalor, F. J.; Ferguson, G.; Ruhl, B.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1983**, 55. [f] (i) Carmona, E.; Marin, J. M.; Poveda, M. L.; Sanchez, L.; Rogers, R. D.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1003. (ii) Carmona, E.; Sanchez, L.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Riester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214. [g] (i) Guzman, E. C.; Wilkinson, G.; Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1978**, 465. (ii) Guzman, C. G.; Wilkinson, G.; Rogers, R. D.; Hunter, W. E.; Zaworotko, M. J.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1980**, 229. [h] Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550. [i] Franke, U.; Weiss, E. *J. Organomet. Chem.* **1979**, *165*, 329. [j] Curtis, M. D.; Real, J. *J. Am. Chem. Soc.* **1986**, *108*, 4668. [k] Kriessl, F. R.; Sieber, W. J.; Wolfgruber, M.; Riede, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 640. [l] Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Chem. Commun.* **1977**, 2297. [m] Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, *1946*. [n] Herrod, J. F.; Malek, A.; Rochon, F. D.; Melanson, R. *Organometallics* **1987**, *6*, 2117. [o] Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049. [p] Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 636. [q] Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, S. C. *J. Am. Chem. Soc.* **1980**, *102*, 5393. [r] (i) Muller, A.; Sarkar, S. *Z. Naturforsch., B* **1978**, *33b*, 1053. (ii) Muller, A.; Seyer, U.; Eltzner, W. *Inorg. Chem. Acta* **1979**, *32*, L65. [s] Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, S. C.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206. [t] Roddock, D. M.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4670. [u] Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1982**, *1*, 869. [v] Churchill, M. R.; Wasserman, H. J. *J. Chem. Soc., Chem. Commun.* **1981**, 274.

the η^2-iminoacyl units occupying one coordination site. The CN vectors are oriented parallel with each other in a head-to-tail fashion. Idealized geometry D would require these vectors to also be parallel with the O–M–O plane, but they are in fact twisted from it by 21.5° (Zr) and 34.5° (Hf).[20] This is predicted on the basis of theoretical studies by Tatsumi et al. and is apparently not a consequence of steric pressure.[97]

Rothwell et al. have also structurally investigated a group 4 compound containing three η^2-iminoacyl ligands, $Zr(OAr\text{-}2,6\text{-}Bu^t{}_2)(\eta^2\text{-}Bu^tNCCH_2Ph)_3$.[20] The central metal environment of this complex is shown in Figure 3. This formally seven-coordinate molecule can again be considered as having pseudotetrahedral geometry. One, unique η^2-iminoacyl lies in a plane containing the Zr–O bond, with the CN vector pointing away. The other two η^2-iminoacyls are coplanar with each other with the carbon atoms in a cis orientation. Their plane is almost exactly perpendicular to the plane containing the first η^2-iminoacyl.[20]

2. *Group 5 Metal Complexes*

There are eight structurally characterized η^2-acyl and η^2-iminoacyl complexes containing group 5 metals. Five of these contain vanadium and three contain tantalum. No structural studies on η^2-acyl or η^2-iminoacyl derivatives of niobium have as yet been reported.

Three of the five vanadium derivatives have the basic stoichiometry $V(CO)_3(L\text{–}L)(\eta^2\text{-}COR)$ and are part of a large number of complexes prepared by Weiss et al.[61,89] The structure of $V(CO)_3(arphos)(\eta^2\text{-}COC_3Ph_3H_2)$ is illustrated in Figure 4 and is typical of the other two

TABLE II. Structural Data for η^2-Iminoacyl Complexes

compd	M—C=N, Å	M—N=C, Å	C=N, Å	d(M—N) − d(M—C), Å	∠M—C=N, deg	ref
$Ru(p\text{-}tolNC\text{-}p\text{-}tol)Cl(CO)(PPh_3)_2$	2.031 (8)	2.123 (7)	1.301 (1)	0.092		*a*
$Cp_2Ti((xy)NCPh)$	2.096 (4)	2.149 (4)	1.280 (6)	0.053	74.7 (2)	*b*
$Cp_2Mo(CO_2)(CH_3CNPh)$	2.106 (5)	2.143 (4)	1.233 (6)	0.037	74.8 (3)	*c*
$Cp_2Zr(OAr)(Bu^tNCCH_2Ph)$	2.208 (5)	2.244 (4)	1.263 (7)	0.036	75.1	*d*
$[Mo(^tBuNCCH_2Ph)(Bu^tNC)_5]Br$	2.14	2.17	1.25	0.030	75	*e*
$[Cp_2V(MeNC(Ph))][Br_4]$	2.030 (4)	2.054 (4)	1.245 (7)	0.024	73.3	*f*
$CpTa(Bu^tNCMe)(ArCCAr)(Me)$	2.10 (1)	2.12 (1)	1.25 (1)	0.02		*g*
$[Cp_2V(p\text{-}tolNC)(NMetol\text{-}p)]I_3$	2.03 (2)	2.04 (1)	1.26 (2)	0.01	72.4 (10)	*h*
$Hf(OAr\text{-}2,6\text{-}Bu^t_2)_2(PhNCMe)_2$	2.209 (6)	2.212 (5)	1.275 (8)	0.003	73.4 (4)	*i*
$Cp_3U((xy)NCNEt_2)$	2.35 (2)	2.35 (2)	1.29 (2)	0	74 (1)	*j*
$Zr(OAr\text{-}2,6\text{-}Bu^t_2)_2(Bu^tNCCH_2Ph)_2$	2.228 (3)	2.221 (3)	1.286 (4)	−0.003	72.9 (2)	*i*
$Zr(OAr\text{-}2,6\text{-}Bu^t_2)(Bu^tNCCH_2Ph)_3$	2.241 (3)	2.211 (3)	1.277 (4)	−0.030	72.0 (2)	
	2.249 (3)	2.257 (3)	1.284 (4)	0.008	73.8 (2)	*i*
	2.251 (3)	2.248 (3)	1.726 (4)	−0.003	73.4 (2)	
$Zr[HB(3,5\text{-}Me_2Pz)_3](OBu^t)(Bu^tNCMe)(Me)$	2.20 (1)	2.194 (8)	1.27 (2)	−0.006	72.8 (6)	*k*
$Ta(OAr\text{-}2,6\text{-}Me_2)_2((xy)NCCH_3)_2(Me)$	2.187 (7)	2.151 (5)	1.281 (8)	−0.036	71.3	*i*
	2.200 (6)	2.165 (5)	1.286 (8)	−0.035	71.4	
$Cp_3U(C_6H_{11}NCMe)$	2.36 (2)	2.40 (2)	1.25 (2)	−0.04		*l*
$Ti(OAr\text{-}2,6\text{-}Ph_2)_2(PhNCCH_2SiMe_3)(CH_2SiMe_3)$	2.086 (6)	2.025 (5)	1.279 (7)	−0.061	74.5 (3)	*i*
$Ti(OAr\text{-}2,6\text{-}Pr^i_2)_2(Bu^tNCCH_2Ph)(CH_2Ph)$	2.096 (5)	2.015 (4)	1.257 (6)	−0.081	75.8 (3)	*i*
$[Cp_2Er(HNCBu^t)]_2$	2.527 (6)	2.312 (5)	1.262 (8)	−0.213	65.6 (3)	*m*
$[Cp_2Y(HCNBu^t)]_2$	2.545 (5)	2.325 (4)	1.275 (6)	−0.220	65.4 (3)	*m*

[a] Roper, W. R.; Taylor, G. E.; Water, J. M.; Wright, L. J. *J. Organomet. Chem.* **1978**, *157*, C27. [b] Van Bolhius, F.; DeBoer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *170*, 299. [c] Adams, R. D.; Chodosh, D. F. *Inorg. Chem.* **1978**, *17*, 41. [d] Steffey, B. D.; Rothwell, I. P., unpublished results. [e] Muller, A.; Seyer, U.; Eltzner, W. *Inorg. Chim. Acta* **1979**, *32*, L65. [f] Carrier, A. M.; Davidson, J. G.; Barefield, E. K.; Van Derveer, D. G. *Organometallics* **1987**, *6*, 454. [g] Curtis, M. D.; Real, J. *J. Am. Chem. Soc.* **1986**, *108*, 4668. [h] Muller, A.; Sarkar, S. *Z. Naturforsch., B* **1978**, *33b*, 1053. [i] Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390. [j] Zanella, P.; Brianese, N.; Casellato, U.; Ossala, F.; Porchin, M.; Rossetto, G.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1987**, 2039. [k] Reger, D. L.; Tarquini, M. E.; Lebioda, L. *Organometallics* **1983**, *2*, 1763. [l] Zanella, P.; Paolucci, G.; Rossetto, G.; Benetollo, F.; Polo, A.; Fischer, R. D.; Bombieri, G. *J. Chem. Soc., Chem. Commun.* **1985**, 96. [m] Evans, W. J.; Hanusa, T. P.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1987**, *6*, 295.

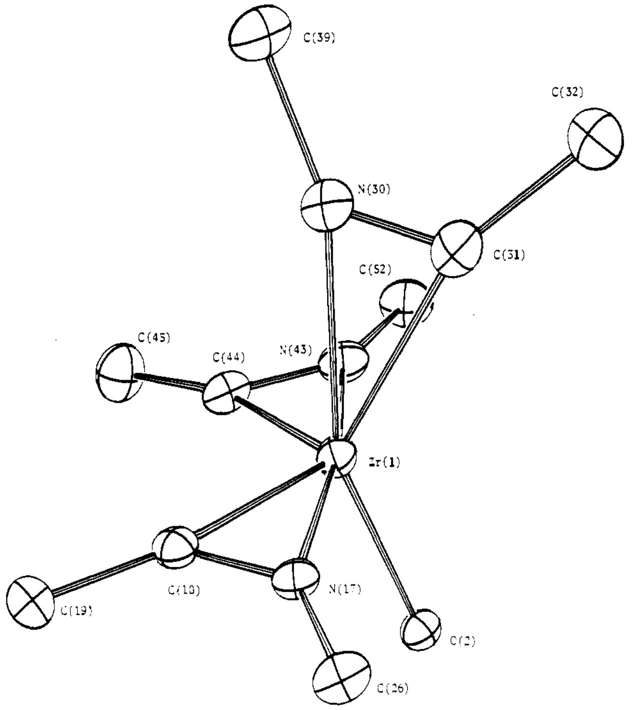


Figure 3. ORTEP view of the central coordination environment in $Zr(OAr\text{-}2,6\text{-}Bu^t_2)(\eta^2\text{-}Bu^tNCCH_2Ph)_3$.

derivatives, $V(CO)_3(dppe)(\eta^2\text{-}COPh)$ and $V(CO)_3(diars)(\eta^2\text{-}COPh\text{-}p\text{-}NMe_2)$. These molecules are best described as having pseudooctahedral geometry with the η^2-acyl ligand occupying one coordination site. In each case the carbonyl ligands are coordinated in a facial arrangement. The acyl oxygen atom is proximal to the bidentate (L–L) ligand and seems to lie in a plane nearly bisecting the L–CH_2–CH_2–L chelate backbone.

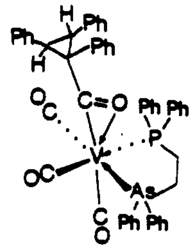


Figure 4. Representation of the coordination in the η^2-acyl compound $(arphos)V(CO)_3(\eta^2\text{-}C_3H_2Ph_3CO)$.

The other two vanadium structures are the cationic η^2-iminoacyl species $[Cp_2V(\eta^2\text{-}p\text{-}tolN(Me)C{=}N\text{-}p\text{-}tol)]I_3$[98] and $[Cp_2V(\eta^2\text{-}MeNCPh)]BF_4$.[91] Both molecules consist of discrete cations and anions. The cations adopt the familiar metallocene bent sandwich configuration, with the planar η^2-iminoacyl group arranged in the equatorial girdle. In the first complex, the iminoacyl carbon to iminoacyl nitrogen and the iminoacyl carbon to substituent nitrogen distances are 1.26 (2) and 1.33 (2) Å, respectively. The closeness of these distances suggests considerable delocalization with high double-bond character for both bonds.[98]

The three tantalum derivatives are $[(CpEt)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHO)$,[75] $CpTa(\eta^2\text{-}Bu^tNCMe)(\eta^2\text{-}ArCCAr)(Me)$,[59] and $Ta(OAr\text{-}2,6\text{-}Me_2)_2(\eta^2\text{-}(xy)NCMe)(Me)$.[20] The first, binuclear complex is best considered as a "stabilized formyl" due to its bridging nature. This is also reflected in the very long C–O distance of 1.496 (14) Å (Table I). The second compound contains both an η^2-iminoacyl and η^2-alkyne ligand with an overall geometry similar to $CpMo(\eta^2\text{-}RCCR)_2L$ molecules.[59] The third compound contains two η^2-iminoacyl moieties. The molecule adopts a structure in which the η^2-iminoacyl groups lie in a plane containing the metal and a

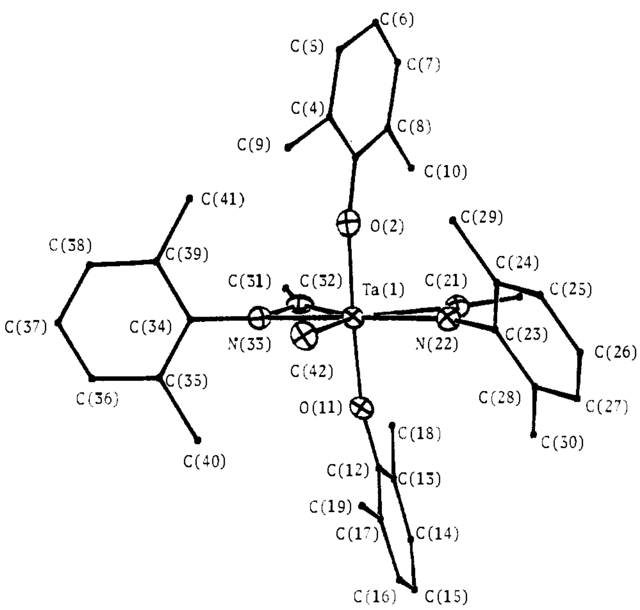


Figure 5. ORTEP view of $Ta(OAr\text{-}2,6\text{-}Me_2)_2(\eta^2\text{-}(xy)NCMe)_2(Me)$ (xy = 2,6-dimethylphenyl).

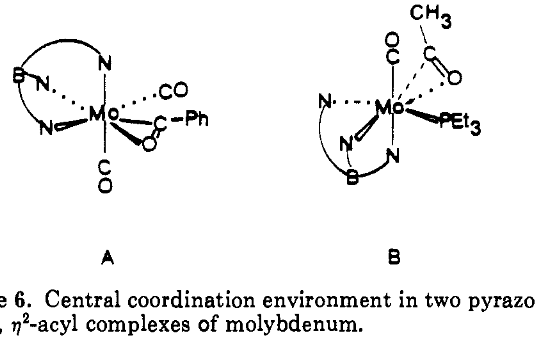


Figure 6. Central coordination environment in two pyrazolylborate, η^2-acyl complexes of molybdenum.

unique, noninserted Ta–Me carbon atom. The aryl oxide oxygen atoms are then arranged perpendicular to this plane and mutually trans. The geometry about the formally seven-coordinate Ta atom can be considered as approaching pentagonal bipyramidal or, due to the small bite of the η^2-iminoacyl groups, trigonal bipyramidal with two of these units in equatorial positions (Figure 5).[20]

3. Group 6 Metal Complexes

Numerous molybdenum and tungsten η^2-acyl and η^2-iminoacyl compounds have been structurally characterized. Only one of these contains an η^2-iminoacyl ligand, $CpMo(CO)_2(\eta^2\text{-MeCNPh})$, and it represents the archetypal example of η^2-iminoacyl bonding, comparing nicely with the related η^1-iminoacyl $CpMo(CO)_2[P(OMe)_3](\eta^1\text{-PhNCMe})$, which has also been structurally characterized.[99]

One type of Mo(II) complex that has been studied by several workers has the general stoichiometry $TpMo(L)(L')(\eta^2\text{-COR})$[48,49] or $Tp^*Mo(L)(L')(\eta^2\text{-COR})$[90] (Tp = hydridotris(pyrazoyl)borate, Tp* = hydridotris(3,5-dimethylpyrazolyl)borate). In each case, the molecules may be viewed as having slightly distorted octahedral structures in which the η^2-acyl group occupies one coordination site. Curtis et al. have reported extensive studies of these complexes.[43,49] Two typical structures, $TpMo(CO)_2(\eta^2\text{-COPh})$ and $TpMo(CO)(PEt_3)(\eta^2\text{-COMe})$, are presented in Figure 6. The Mo–N bond distances show interesting variations, depending on the nature of L. On the basis of these variations, the following order of trans influence was deduced: CO > PEt_3 > η^2-COR ≈ $P(OMe)_3$. Although metal electron density was found to greatly influence the Mo–C and C–O distances in the carbonyl ligands, very little influence was noticed on the η^2-acyl ligand. However, the Mo–C(acyl) distances [2.01 Å (av)] suggest significant double-bond character as mentioned earlier. Theoretical calculations by the EHMO method supported this conclusion.[48,49]

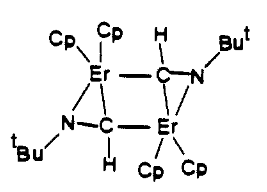


Figure 7. $[Cp_2Er(\eta^2\text{-HCNBu}^t)]_2$.

Three other group 6 η^2-acyl complexes that are also six-coordinate are the dimers $[M(\mu\text{-Cl})(CO)_2(PMe_3)(\eta^2\text{-COCH}_2SiMe_3)]_2$ (M = Mo, W) (Scheme V) and the monomer $MoCl(PMe_3)_3(CO)(\eta^2\text{-COCH}_2SiMe_3)$.[46,47]

Finally, a crystal structure of the W(IV) molecule $CpWCl_2(CO)(\eta^2\text{-COEt})$ has been reported.[50]

4. Group 8 Metal Complexes

The 18-electron η^2-acyl, η^2-iminoacyl, and η^2-thioacyl derivatives of Ru and Os reported by Roper et al. have related structures.[68] Hence, generalizing the stoichiometries as $M(\eta^2\text{-CXR})(Y)(L)(PPh_3)_2$ (X = O, NR, S; Y = anionic ligand; L = CO or CNR), one finds a trigonal-bipyramidal arrangement of ligands around the metal center with the η^2-CXR occupying one equatorial position. The two phosphine ligands are in mutually trans axial positions.[68] The iron compound $Fe(\eta^2\text{-COPr}^i)I(CO)(PEt_3)_2$ adopts an identical structure,[69c] while the stoichiometrically related iron η^2-acyl compound $Fe(\eta^2\text{-CO(mes)})Br(CO)(dippe)$ adopts a similar structure, except now the chelating phosphine donor atoms are forced to occupy one axial and one equatorial position.[69b] In all of the above 18-electron compounds the CX vector lies within the equatorial plane.

5. Lanthanide and Actinide Metal Complexes

The only lanthanide complex structurally characterized is a dimeric "stabilized" formimidoyl compound of erbium, $[Cp_2Er(HCNBu^t)]_2$.[77] The analogous group 3 yttrium complex, $[Cp_2Y(HCNBu^t)]_2$, has also been structurally characterized.[77] The structure of the erbium derivative is shown in Figure 7. The unit cell of the erbium complex actually contains two crystallographically independent centrosymmetric dimers. These molecules are formally similar to bent metallocene complexes with three additional ligands. The overall structure and orientation of the formimidoyl ligands in the yttrium molecule and two erbium conformers are similar. However, the relative positions of the cyclopentadienyl rings as measured by twist angle are found to vary. The yttrium molecule and one erbium conformer have twist angles of 6.4° and 2.2°, respectively. These are closer to an eclipsed arrangement (0°) than a staggered arrangement (36°). In the same unit cell, however, the other erbium conformer has a twist angle of 36.2°. This behavior is attributed to

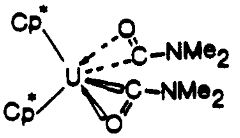


Figure 8. Coordination environment in the bis(η^2-carbamoyl) $Cp^*_2U(\eta^2\text{-}Me_2NCO)_2$.

crystal packing forces.[77] The formimidoyl ligands are considered "stabilized" via bridging, η^2-bonding, but the C–N bond lengths (1.26–1.29 Å) are not elongated as in the Ta-stabilized formyl complex mentioned earlier.[75]

The structurally characterized η^2-acyl, η^2-iminoacyl and η^2-carbamoyl actinide metal complexes fall into four basic stoichiometries: $Cp^*_2ThCl(\eta^2\text{-}RCO)$, $Cp^*_2ThCl(\eta^2\text{-}R_2NCO)$, $Cp^*_2U(\eta^2\text{-}R_2NCO)_2$, and $Cp_3U(\eta^2\text{-}RCX)$ (X = O, NR′). In the first category Marks et al. have reported the structures of $Cp^*_2ThCl(\eta^2\text{-}Bu^tCH_2CO)$[38] and $Cp^*_2ThCl(\eta^2\text{-}PhCO)$.[35] The thorium coordination in both cases involves the familiar bent sandwich configuration with the η^2-acyl group oriented within the equatorial girdle. As with the group 4 metal compounds, two isomers are possible and indeed these two compounds adopt solid-state structures A and B (Scheme XI), respectively. Consistent with the implied similarity in energy between the two isomers is the fact that the stoichiometrically related η^2-carbamoyl $Cp^*_2ThCl(\eta^2\text{-}Et_2NCO)$[81] shows both present in the unit cell. The high oxophilicity of these actinide metals is evident in the small number observed for Δ (Table I).

A second type of actinide complex to be structurally characterized is the bis(η^2-carbamoyl) $Cp^*_2U(\eta^2\text{-}CONMe_2)_2$.[81] The structure of this molecule is illustrated in Figure 8. Referring to Scheme XII, one sees that this molecule adopts ground-state structure A. The η^2-carbamoyl ligands are oriented at angles of 13.2° and 15.4° with the equatorial girdle plane, with the carbon atoms proximal to each other. This slight distortion appears to result from nonbonded repulsion between the methyl carbons on the planar η^2-carbamoyl groups.

The final category of structurally characterized actinide η^2-acyl and η^2-iminoacyl complexes consists of $Cp_3U(\eta^2\text{-}RCX)$ (X = O, NR′) compounds. Three such compounds are known, $Cp_3U((xy)NCNEt_2)$,[83] $Cp_3U(C_6H_{11}NCMe)$,[41] and $Cp_3U[(OCCH)PMePh_2]$.[100] The first two molecules are very similar in structure, with the overall geometry being pseudotetrahedral. In the iminocarbamoyl derivative, two of the cyclopentadienyl ligands are symmetrically inclined to the U-CNCN plane, which perpendicularly intersects the third cyclopentadienyl ring. A similar structural feature is observed in the iminoacyl complex where the corresponding mirror plane is determined by space group symmetry. In both the η^2-carbamoyl and the η^2-carboxyphosphide complexes, significant amounts of carbon–nitrogen (phosphorus) multiple bonding is structurally evident.

IV. Solution Structure and Spectroscopy of η^2-Acyl, η^2-Iminoacyl, and Related Functional Groups

A. Spectroscopic Data

The two pieces of spectroscopic data that allow an assessment of the acyl/iminoacyl coordination properties in solution are ν(CX), the stretching frequency of the acyl/iminoacyl C═X (X = O, NR′) bond, and the ^{13}C NMR resonance of the iminoacyl/acyl carbon. Tables III and IV list the d-block, lanthanide, and actinide metal complexes for which one or both of these values are reported, along with the corresponding values.

The C═O stretching vibration in η^2-acyls ranges from 1453 cm^{-1} in $Cp^*Th(\eta^2\text{-}COCH_2Bu^t)(OCHBu^t_2)$[37] to 1625 cm^{-1} in $Cp_2Ti(\eta^2\text{-}COCH_2Ph)(Cl)$.[12] The abnormally low value of 1350 cm^{-1} in $Cp^*HfCl_2(\eta^2\text{-}COPBu^t_2)$ apparently arises from partial double-bond interaction of the acyl carbon with the phosphorus, concomitantly giving the C–O some single-bond character. The analogous C═N stretching vibration in the η^2-iminoacyl complexes ranges from 1510 cm^{-1} in the iminophosphide $Cp_3U(\eta^2\text{-}(xy)NCPPh_2)$[83] to 1720 cm^{-1} in $CpMo(CO)_2(\eta^2\text{-}MeCNMe)$.[57,58]

For η^2-acyl complexes ν(C═O) is typically lower than found for related η^1-acyl complexes. For instance, compare $CpW(CO)_3(\eta^1\text{-}COEt)$,[101] ν(CO) = 1640 cm^{-1}, with $CpW(CO)(C_2H_2)(\eta^2\text{-}COMe)$,[51] ν(CO) = 1591 cm^{-1}, and $Cp_2Ti(\eta^1\text{-}COCH_2CMeCMe)$, ν(CO) = 1615 cm^{-1}, with $Cp_2Ti(\eta^2\text{-}CO\text{-}trans\text{-}CMeCHMe)(SC_6H_5)$, ν(CO) = 1563 cm^{-1}.[31] The lowest stretching frequencies occur for η^2-acyl complexes containing high-valent metals, and particularly for the highly oxophilic actinide elements. This has been attributed to the participation of a "carbene-like" resonance form[34,35] or, as more recent studies suggest, the participation of a "carbenium ion like" acceptor orbital on the undistorted η^2-acyl structure.[102]

The ν(C═N) stretching values in η^2-iminoacyl complexes have been a somewhat inconsistent parameter for the assignment of a bonding mode. The $\bar{\nu}$(C═N) values for η^1-iminoacyl groups bound to electron-rich, later transition metal metal systems typically lie in the 1580–1680-cm^{-1} range.[20,103] Many η^2-iminoacyl ν(C═N) values also fall within this range. In the molybdenum systems, first studied by Adams et al., it was found that the stretching frequency increased upon going from η^1- to η^2-coordination.[57,58]

Another characteristic parameter for the assignment of the acyl/iminoacyl bonding mode in diamagnetic compounds is the acyl/iminoacyl carbon ^{13}C NMR resonance position. From Tables III and IV, it can be seen that these values fall in the ranges of 248–392 and 195–268 ppm for η^2-acyls and η^2-iminoacyls, respectively. Adams has shown that the iminoacyl carbon in $CpMo(CO)_2(\eta^2\text{-}MeCNMe)$ resonates approximately 40 ppm downfield of the corresponding resonance in $CpMo(CO)_2[P(OMe)_3](\eta^1\text{-}MeCNPh)$.[57,58] The shift of the η^2-acyl/iminoacyl carbon resonance to lower field has again been used to argue for the importance of the oxy/amido–carbene resonance to these compounds.[34]

B. Solution Structure and Fluxionality

On the basis of the solid-state structural studies referred to above, it is to be expected that solution studies may also indicate the presence of isomers due to the orientation of the η^2-acyl or related functionality. Furthermore, in favorable circumstances solution studies also allow not only measurements of the relative thermodynamic stabilities of such isomers but also estimates of the rates of interconversion. Indeed, this

TABLE III. Selected Spectroscopic Data on η^2-Acyl Complexes

compd	ν(C=O), cm^{-1}	^{13}C(*C*=O), ppm	ref
Cp$_2$Ti[CO-*trans*-C(CH$_3$)CHCH$_3$]	1482		*a*
Cp$_2$Ti[CO-*trans*-C(CH$_3$)CHCH$_3$](SC$_6$H$_5$)	1563		*a*
Cp$_2$Ti(CO-*o*-tol)	1470		*b*
Cp$_2$Ti(CO-*o*-tol)(Cl)	1570–1580		*b*
Cp$_2$Ti(CO-*o*-tol)(SC$_6$H$_5$)	1570–1580	286.5	*b*
Cp$_2$Ti(COC$_5$H$_{11}$-*neo*)[(CO)$_3$MoCp]		299	*c*
Cp$_2$Ti(COMe)[(CO)$_3$MoCp]	1548		*c*
Cp$_2$Ti(COCH$_3$)(Cl)	1620		*d*
Cp$_2$Ti(COPh)(Cl)	1580		*d*
Cp$_2$Ti(COEt)(I)	mull 1605 soln 1610		*e*
Cp$_2$Ti(COEt)(Cl)	mull 1603 soln 1615		*e*
Cp$_2$Ti(COCH$_2$Ph)(Cl)	1625		*e*
Cp$_2$Ti(COMe)(GePh$_3$)	1600		*f*
Cp$_2$Zr(COSiMe$_3$)(Cl)	1489	391.6	*g*
Cp$_2$Zr[CO(CHPPh$_3$)](Cl)	1550		*h*
Cp$_2$Zr(COSiMe$_3$)(OTf)	1500	389.7	*i*
Cp$_2$Zr(COSiMe$_3$)[Si(SiMe$_3$)$_3$]	1503	387.3	*j*
Cp$_2$Zr(COCH$_3$)[Si(SiMe$_3$)$_3$]	1505	312.3	*j*
Cp$_2$Zr(COCH$_2$Bu^t)(Cl)	1550	318.7	*k*
Cp$_2$Zr(COCH$_2$SiMe$_3$)(Cl)	1515	317.2	*k*
Cp$_2$Zr(COCH$_2$Bu^t)(CH$_2$Bu^t)	1545	322.9	*k*
Cp$_2$Zr(COCH$_2$SiMe$_3$)(CH$_2$SiMe$_3$)	1500	317.2	*k*
Cp$_2$Zr[COCH(SiMe$_3$)]$_2$(Me)	1470		*k*
Cp$_2$Zr(COCH$_3$)(CH$_3$)	1545		*l*
Cp$_2$Zr(COCH$_2$Ph)(CH$_2$Ph)	1540		*l*
Cp$_2$Zr(COPh)(Ph)	1510		*l*
Cp$_2$Zr(CO-*p*-tol)(*p*-tol) distal	1480	300	*m*
Cp$_2$Zr(CO-*p*-tol)(*p*-tol) proximal	1505	301	*m*
Cp$_2$Zr(COMe)[(CO)$_3$MoCp]	1590	136.5	*n*
Cp$_2$Zr(COC$_6$H$_{13}$)(Cl)	1550		*o*
Cp*$_2$Zr(COMe)(Me)	1545		*p*
Cp$_2$Hf(COMe)(Me)	1550		*l*
Cp$_2$Hf(COCH$_2$Ph)(CH$_2$Ph)	1530		*l*
Cp$_2$Hf(COPh)(Ph)	1500		*l*
Cp*HfCl$_2$(COPBu$^t{}_2$)	1350		*q*
Cp$_2$V(COMe)(CO)	1605		*r*
Cp$_2$V(COCH$_2$Ph)(CO)	1615		*r*
V(CO)$_3$(dppe)(COPh)	1518		*s*
V(CO)$_3$(diars)(COC$_6$H$_4$-*p*-NMe$_2$)	1530		*s*
V(CO)$_3$(dppe)(COC$_3$H$_5$)	1541		*s*
V(CO)$_3$(dppe)(COPh-4-F)	1520		*s*
V(CO)$_3$(dppe)(COPh-4-Cl)	1523		*s*
V(CO)$_3$(dppe)(COPh-4-Me)	1521		*s*
V(CO)$_3$(dppe)(COPh-2,4,6-Me$_3$)	1540		*s*
V(CO)$_3$(dppe)(COPh-*p*-NMe$_2$)	1505		*s*
V(CO)$_3$(dppe)(COPh-4-MeO)	1523		*s*
V(CO)$_3$(dppp)(COC$_3$H$_5$)	1525		*s*
V(CO)$_3$(dppp)(COPh-*p*-NMe$_2$)	1525		*s*
V(CO)$_3$(dppp)(COPh-4-OMe)	1510		*s*
V(CO)$_3$(dppp)(COPh-2-OMe)	1530		*s*
V(CO)$_3$(arphos)(COPh-*p*-NMe$_2$)	1521		*s*
V(CO)$_3$(arphos)(COPh-4-OMe)	1521		*s*
V(CO)$_3$(diars)(COPh-4-OMe)	1525		*s*
V(CO)$_3$(diars)(COPh-2-OMe)	1540		*s*
[MoCl(COCH$_2$SiMe$_3$)(CO)$_2$PMe$_3$]$_2$	1585		*t*
MoCl(COCH$_2$SiMe$_3$)(CO)(PMe$_3$)$_3$	1500		*u*
TpMo(CO)$_2$(COMe)	1570	265	*v*
TpMo(CO)$_2$(COPh)		254	*v*
TpMo(CO)[P(OMe)$_3$](COMe)	1508	267.6	*v*
TpMo(CO)(PEt$_3$)(COMe)	1510	253.6	*v*
CpW(CO)(C$_2$H$_2$)(COMe)	soln 1591 KBr 1573		*w*
CpW[P(OMe)$_3$](C$_2$H$_2$)(COMe)	1525		*w*
[WCl(COCH$_2$SiMe$_3$)(CO)$_2$(PMe$_3$)]$_2$	1530		*w*
Cp*$_2$Th(OCHBu$^t{}_2$)(COMe)		362.5	*y*
Cp*$_2$Th(OCHBu$^t{}_2$)(COBu^n)	1479	356.6	*y*
Cp*$_2$Th(OBu$^t{}_2$)(COCH$_2$Bu^t)	1472	361.9	*y*
Cp*$_2$Th(OCHBu$^t{}_2$)(COCH$_2$Bu^t)	1453	359.5	*y*
Cp*$_2$Th(OCHBu$^t{}_2$)(COH)	1477	372	*y*
Cp*$_2$Th(OC$_6$H$_3$-2,6-Bu$^t{}_2$)(COH)		360	*y*
Cp*$_2$Th(Cl)(COCH$_2$Bu^t)	1469	360.2	*y*
Cp$_3$Th(COCH$_2$Bu^t)	1492	356.7	*y*
Cp*$_2$Th(Cl)(CONMe$_2$)	1546		*z*
Cp*$_2$Th(Cl)(CONEt$_2$)	1516	248.5	*z*
Cp*$_2$Th(NMe$_2$)(CONMe$_2$)	1521		*z*
Cp*$_2$Th(CONMe$_2$)$_2$	1523		*z*
Cp*$_2$Th(NMe$_2$)(COCH$_3$)	1483		*z*
Cp$_3$U(COBu^t)	1490		*aa*
Cp$_3$U(COPr^i)	1493		*aa*
Cp$_3$U(COBu^n)	1495		*aa*
Cp$_3$U(COEt)	1504		*aa*
Cp$_3$U(COMe)	1504		*aa*
Cp$_3$U(CONEt$_2$)	1521		*z*
Cp*$_2$U(Cl)(CONMe$_2$)	1559		*z*
Cp*$_2$U(Cl)(CONEt$_2$)	1537		*z*
Cp*$_2$U(NMe$_2$)(CONMe$_2$)	1521		*z*
Cp*$_2$U(NEt$_2$)(CONEt$_2$)	1491		*z*
Cp*$_2$U(CONMe$_2$)$_2$	1529		*z*
Cp*$_2$U(CONEt$_2$)$_2$	1499		*z*
Cp$_2$Lu(COBu^t)	1490	380.6	*ab*
Fe(COPr^i)I(CO)(PEt$_3$)$_2$	1586	286.1	*ac*
Fe(CO-mes)Br(CO)(dippe)	1525	260.0	*ad*
Fe(COCH$_2$CMe$_3$)Cl(CO)(dippe)	1596		*ad*
Fe(COCH$_2$CMe$_3$)Br(CO)(dippe)	1591	277.5	*ad*
Ru(COMe)I(CO)(PPh$_3$)$_2$	1599		*ae*
Ru(CO-*p*-tol)I(CO)(PPh$_3$)$_2$	1550		*ae*
Os(CO-*p*-tol)Cl(CH$_2$)(PPh$_3$)$_2$	1506		*af*

[a] Keli, E.; Teuben, J. H. *J. Organomet. Chem.* 1981, *222*, 79. [b] DeBoer, E. J. M.; Ten Cate, L. C.; Staring, A. G. J.; Teuben, J. H. *J. Organomet. Chem.* 1979, *181*, 61. [c] DeBoer, E. J. M.; De With, J. *J. Organomet. Chem.* 1987, *320*, 289. [d] Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Chem. Commun.* 1977, 2297. [e] Fachinetti, G.; Floriani, C. *J. Organomet. Chem.* 1974, *71*, C5. [f] Herrod, J. F.; Malek, A.; Rochon, F. D.; Melanson, R. *Organometallics* 1987, *6*, 2117. [g] Tilley, T. D. *J. Am. Chem. Soc.* 1985, *107*, 4084. [h] Baldwin, J. C.; Kedar, N. L.; Strouse, C. E.; Kaska, W. C. *Naturforsch. B., Anorg. Chem. Org. Chem.* 1980, *35B*, 1289. [i] Tilley, T. D. *J. Am. Chem. Soc.* 1985, *107*, 4084. [j] Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* 1987, *109*, 2049. [k] Jeffrey, J.; Lappert, M. F.; Luong-Thi, N. T.; Webb, M.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* 1981, 1593. [l] Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* 1977, 1946. [m] Erker, G.; Rosenfeldt, F. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 605. [n] Longato, B.; Norton, J. R.; Huffman, J. C.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* 1981, *103*, 209. [o] Bertelo, C. A.; Schwartz, J. *J. Am. Chem. Soc.* 1975, *77*, 228. [p] Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* 1978, *100*, 2716. [q] Roddock, D. M.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* 1985, *107*, 4670. [r] Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* 1976, 203. [s] Schiemann, J.; Weiss, E. *J. Organomet. Chem.* 1983, *255*, 179. [t] (i) Guzman, E. C.; Wilkinson, G.; Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* 1978, 465. (ii) Guzman, C. G.; Wilkinson, G.; Rogers, R. D.; Hunter, W. E.; Zaworotko, M. J.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* 1980, 229. [u] Carmona, E.; Sanchez, L.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Riester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* 1984, *106*, 3214. [v] Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *J. Am. Chem. Soc.* 1986, *108*, 1550. [w] Alt, H. G. *J. Organomet. Chem.* 1977, *127*, 349. [x] Carmona, E.; Marin, J. M.; Poveda, M. L.; Sanchez, L.; Rogers, R. D.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* 1983, *1003*. [y] Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* 1984, *106*, 7051. [z] Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, S. C.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* 1981, *103*, 2206. [aa] Paolucci, G.; Rossetto, G.; Zanella, P.; Yunlu, K.; Fischer, R. O. *J. Organomet. Chem.* 1984, *272*, 363. [ab] Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* 1981, 706. [ac] Birk, R.; Berke, H.; Hunter, G.; Zsolani, L. *J. Organomet. Chem.* 1986, *309*, C18. [ad] Hermes, A. R.; Girolami, G. S. *Organometallics* 1988, *7*, 394. [ae] Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* 1979, *182*, C46. [af] Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Shepard, W. E. B.; Wright, L. J. *J. Chem. Soc., Chem. Commun.* 1987, 563.

type of behavior was observed in early studies by Lappert,[18] Adams,[58] Erker,[15,104] and other.[51] Lappert observed NMR and infrared signals from two species in solutions of Cp$_2$Zr(X)[η^2-(SiMe$_3$)$_2$CHCN-*p*-tol]. He

TABLE IV. Selected Spectroscopic Data on η^2-Iminoacyl Complexes

compd	ν(CN), cm^{-1}	$^{13}C(C{=}N)$, ppm	ref
$Cp_2Ti((xy)NCPh)$	1573		*a*
$Cp_2Ti((xy)NC\text{-}o\text{-}tol)$	1560		*a*
$Cp_2Ti((xy)NCPh)(I)$	1665	215	*a*
$Cp_2Ti((xy)NCPh)(SC_6H_5)$	1655	230	*a*
$Cp_2Ti((xy)NC\text{-}o\text{-}tol)(I)$	1665		*a*
$Cp_2Ti((xy)NC\text{-}o\text{-}tol)(SC_6H_5)$	1655	226.6	*a*
$Cp_2Ti((xy)NCCH_2CHCH_2)$	1578		*b*
$Cp_2Ti((xy)NCCH_2CHCHCH_3)$	1585		*b*
$Cp_2Ti((xy)NCCH_3)$	1578		*c*
$Cp_2Ti((xy)NCCH_3)(I)$	1677		*c*
$Cp_2Ti((xy)NCCH_3)(SC_6H_5)$	1662	231.2	*c*
$Cp_2Ti[(xy)NCC(CH_3)CHCH_3\text{-}trans]$	1562		*d*
$Cp_2Ti((xy)NCCH_2CHCH_2)(SC_6H_5)$	1682		*b*
$Cp_2Ti((xy)NCCH_2CHCHCH_3)(SC_6H_5)$	1680		*b*
$Cp_2Ti((xy)NCC_2H_5)$	1570		*e*
$Cp_2Ti((xy)NCBu^s)$	1572		*e*
$Cp_2Ti((xy)NCBu^t)$	1578		*e*
$Cp_2Ti((xy)NCC_2H_5)(SC_6H_5)$	1662		*e*
$Cp_2Ti((xy)NCBu^n)(SC_6H_5)$	1670		*e*
$Cp_2Ti((xy)NCBu^s)(SC_6H_5)$	1675		*e*
$Cp_2Ti((xy)NCBu^t)(SC_6H_5)$	1654		*e*
$Cp_2Ti(C_6H_{11}NCMe)(Me)$	1680		*f*
$Cp_2Ti(C_6H_{11}NCC_6F_5)(Me)$	1640	215.7	*g*
$Cp_2Ti(C_6H_{11}NCC_6H_5)(Me)$	1670	224.7	*g*
$Cp_2Ti(C_6H_{11}NCC_6H_5)(Cl)$	1685	216.6	*g*
$Ti(OAr\text{-}2,6\text{-}Pr^i{}_2)_2((xy)NCCH_2Ph)_2$	1580	237.1	*h*
$Ti(OAr\text{-}2,6\text{-}Pr^i{}_2)_2(Bu^tNCCH_2Ph)(CH_2Ph)$	1560	230.5	*i*
$Ti(OAr\text{-}2,6\text{-}Ph_2)_2(PhNCCH_2SiMe_3)\text{-}(CH_2SiMe_3)$	1565	240.7	*i*
$Ti(OAr\text{-}2,6\text{-}Ph_2)_2((xy)NCCH_2SiMe_3)\text{-}(CH_2SiMe_3)$	1560	242.4	*i*
$Ti(OAr\text{-}2,6\text{-}Ph_2)_2((xy)NCCH_2Ph)(CH_2Ph)$	1595	238.9	*i*
$Ti(OAr\text{-}2,6\text{-}Ph_2)_2((xy)NCCH_2Ph)_2$	1587	241.1	*i*
$Cp_2Zr((xy)NCSiMe_3)(Cl)$	1558	275.6	*j*
$Cp_2Zr[(xy)NCSi(SiMe_3)_3]$	1555	267.6	*j*
$Cp_2Zr[p\text{-}tolNCCH(SiMe_3)_2](Cl)$	1540	238	*k*
	1520	233	
$Cp_2Zr[p\text{-}tolNCCH(SiMe_3)_2](Me)$	1530	241.6	*k*
		237.9	
$Cp_2Zr(p\text{-}tolNCCH_2SiMe_3)(CH_2SiMe_3)$	1578	242.5	*k*
$Cp_2Zr(p\text{-}tolNCCH_2Bu^t)(CH_2Bu^t)$	1578	245.8	*k*
$Cp_2Zr(CH_2Ph)((xy)NCCH_2Ph)$		246.5	*l*
$Zr(OAr\text{-}2,6\text{-}Bu^t{}_2)_2((xy)NCMe)_2$	1579	245.2	*h*
$Zr(OAr\text{-}2,6\text{-}Bu^t{}_2)_2((xy)NCCH_2Ph)(CH_2Ph)$	1530	246.3	*i*
$Zr(OAr\text{-}2,6\text{-}Bu^t{}_2)_2((xy)NCCH_2Ph)_2$	1560	239.0	*i*
$Zr(OAr\text{-}2,6\text{-}Bu^t{}_2)_2(Bu^tNCCH_2Ph)$	1570	244.3	*i*
$Zr(OAr\text{-}2,6\text{-}Bu^t{}_2)(Bu^tNCCH_2Ph)_3$	1560	256.6	*i*
$Zr(OAr\text{-}2,6\text{-}Bu^t{}_2)((xy)NCCH_2Ph)_3$	1580	247.1	*i*
		262.3	
$Tp^*Zr(OBu^t)(Bu^tNCMe)(Me)$	1542	243.6	*m*
$Tp^*Zr(OBu^t)(Bu^tNCCH_2Ph)(CH_2Ph)$	1539	244.0	*m*
$Cp_2Hf(CH_2Ph)((xy)NCCH_2Ph)$		254.1	*l*
$Hf(OAr\text{-}2,6\text{-}Bu^t{}_2)_2(PhNCMe)_2$	1550	255.0	*i*
$Hf[(Me_3Si)_2N]_2(Bu^tNCMe)_2$	1565		*n*
$Hf[(Me_3Si)_2N]_2(Bu^tNCEt)_2$	1565	262	*n*
$[Cp_2V(p\text{-}tolN(Me)CN\text{-}p\text{-}tol)][I_3]$	1680		*o*
$[Cp_2V(MeNCPh)][BF_4]$	1745		*p*
$Ta(OAr\text{-}2,6\text{-}Me_2)_2((xy)NCMe)_2(Me)$	1590	239.6	*i*
$Ta(OAr\text{-}2,6\text{-}Me_2)_2(2,6\text{-}Pr^i\text{-}PhNCMe)_2(Me)$	1585	240.8	*i*
$Ta(OAr\text{-}2,6\text{-}Me_2)_2((xy)NCH_2Ph)_2(CH_2Ph)$	1580	239.7	*i*
$Ta(OAr\text{-}2,6\text{-}Me_2)_2(2,6\text{-}Pr^i\text{-}PhNCCHPh)_2(CH_2Ph)$	1590	240.1	*i*
$Ta(OAr\text{-}2,6\text{-}Me_2)_3((xy)NCCH_2Ph)_2$	1568	241.7	*i*
$CpTa(MeCNBu^t)(ArCCAr)$		241.1	*q*
$[Mo(Bu^tNCCH_3)(Bu^tNC)_5]I$	1758	196–198	*r*
$[Mo(Bu^tNCCH_2Ph)(Bu^tNC)_5]Br$	1755	196–198	*r*
$CpMo(CO)_2(MeCNPh)$	1670		*s*
$CpMo(CO)_2(MeCNMe)$	1720	195.15	*s*
$(CpMe)Mo(CO)_2(MeNCMe)$		196.99	*t*
$[(Cp)_2Y(HCNBu^t)]_2$	1540	217.0	*u*
$[(CpMe)_2Y(HCNBu^t)]_2$	1532	218.1	*u*
$[(Cp)_2Er(HCNBu^t)]_2$	1535		*u*
$Cp_3U(C_lH_{11}NCMe)$	1570		*v*
$Cp_2U(NEt_2)(C_6H_{11}NCNEt_2)$	1645		*w*
$Cp_2U(NEt_2)((xy)NCNEt_2)$	1640		*w*
$Cp_2U(C_6H_{11}NCNEt_2)_2$	1650		*w*
$Cp_2U((xy)NCNEt_2)_2$	1645		*x*
$Cp_2U(C_6H_{11}NCNEt_2)(Cl)$	1690		*x*
$Cp_2U(NEt_2)(C_6H_{11}NCMe)$	1625		*x*
$Cp_3U(C_6H_{11}NCBu^n)$	1598		*y*
$Cp_3U(Bu^tNCBu^n)$	1596		*y*
$Cp_3U((xy)NCBu^n)$	1598		*y*
$Cp_2U(Bu^tNCMe)(Me)$	1610		*y*
$Cp_2U(Bu^tNCMe)(Cl)$	1608		*y*
$Cp_2U(Bu^tNCBu^n)(Cl)$	1608		*y*
$Cp_3U((xy)NCNEt_2)$	1535		*x*
$Cp_3U((xy)NCPPh_2)$	1510		*x*
$Ru(p\text{-}tolNC\text{-}p\text{-}tol)Cl(CO)(PPh_3)_2$	1654		*z*

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attributed it to restricted rotation of the bulky η^2-iminoacyl. Adams noted temperature-dependent NMR spectra for solutions of $CpMo(CO)_2(\eta^2\text{-}MeCNMe)$.[58] Analysis of the spectroscopic data led to the conclusion that restricted rotation of the η^2-iminoacyl ligand is taking place and not a polytopal rearrangement at the metal atom that exchanges carbonyls. Erker performed kinetic studies on the carbonylation of Cp_2ZrMe_2.[15] The initially formed product contains an η^2-acyl ligand oriented in a distal fashion (Scheme XI). When this product is warmed to −53 °C, isomerization takes place, giving the thermodynamic proximal conformer. In the case of $Cp_2Zr(Me)(\eta^2\text{-}COMe)$, rearrangement takes place at −123 °C with a first-order rate constant of $(9.03 \pm 0.4) \times 10^{-5}\ s^{-1}$.[15] In the past several years many more examples of this type of behavior have been noted and in many cases thermodynamic data obtained (Table V). In some cases, the rotation is extremely facile and even at low temperature is too fast to be frozen out.[20] Reger has observed in $Tp^*Zr(OBu^t)(\eta^2\text{-}RCNBu^t)(R)$ (R = Me, CH_2Ph)[56] complexes that two isomers can be detected in solution. However, heating the solutions to +70 °C gave no indication of interconversion on the NMR time scale. Coalescence temperature measurements have allowed the estimation of activation barriers for η^2-function rotation in uranium carbamoyls[36,81] as well as for a number of mixed aryl oxide η^2-iminoacyls of the group 4 metals.[20]

TABLE V. Thermodynamics Data for η^2-Acyl/η^2-Iminoacyl Rotation

complex	T_{isom}, °C	ΔG^*, kcal/mol	ref
$Cp_2Zr(Me)(COMe)$	−123	11.4	*a*
$Cp_2Zr(Ph)(COPh)$	−59	15.2	*a*
$Cp_2Zr(p\text{-tol})(CO\text{-}p\text{-tol})$	−59	15.6	*a*
$Cp_2Zr(p\text{-anisyl})(CO\text{-}p\text{-anisyl})$	−63	15.6	*a*
$Cp_2Zr(Me)(COPh)$	−53	15.1	*a*
$Cp_2Zr(Cl)(COPh)$	−70		*a*
$Cp_2Zr(Br)(COPh)$	−65		*a*
$Cp_2Zr(SPh)(COPh)$	−57		*a*
$Cp^*_2U(CONMe_2)(Cl)$	−80	8.9 ± 0.5	*b, c*
$Cp^*U(CONEt_2)(Cl)$	−70	8.9 ± 0.5	*b, c*
$Ti(OAr\text{-}2,6\text{-}Ph_2)_2((xy)NCCH_2Ph)_2$	−65	10.3 ± 0.5	*d*
$Zr(OAr\text{-}2,6\text{-}Bu^t_2)_2((xy)NCCH_2Ph)_2$	−40	11.4 ± 0.5	*d*

[a] Erker, G. *Acc. Chem. Res.* 1984, *17*, 103. [b] Fagan, P. J.; Maata, E. A.; Marks, T. J. *ACS Symp. Ser.* 1980, *No. 152*, 53. [c] Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, S. C.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* 1981, *103*, 2206. [d] Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* 1987, *109*, 390.

The isomerization process can be viewed as occurring either via a simple rotation of the η^2-fragment about its midpoint or by an η^2–η^1–η^2 sequence, involving essentially initial complete dissociation of the heteroatom from the metal center followed by rotation and recoordination. Hoffmann et al. have carried out extensive theoretical studies on the η^2-acyl complex $Cp_2Zr(Me)(\eta^2\text{-}COMe)$ using the EHMO method.[102,105] They found that the isomerization process from η^2-O-outside to η^2-O-inside proceeded through an η^2–η^1–(rotation)–η^2 motion. However, non-cyclopentadienyl group 4 metal complexes such as $M(OAr)_x(\eta^2\text{-}RCNR')_{4-x}$ compounds possess less electronic restrictions than the corresponding Cp_2M derivatives, and hence a direct η^2-rotation may be available in these cases.[20]

In related studies of $TpMo(CO)_2(L)(\eta^2\text{-}COR)$ complexes, Curtis et al. observed a low-energy fluxional process that averages the effective symmetry to C_s.[48] The minimal motion that time averages the molecule is a libration of the η^2-COR group coupled with a bending motion.

Another type of fluxionality that has been observed in η^2-carbamoyl, η^2-carboxyphosphide, and η^2-iminocarbamoyl complexes is the presence of restricted rotation about the C_{acyl}–YR_2 bond (Y = N, P).[40,81–86] In the molecules $Cp^*_2M(\eta^2\text{-}CONR_2)(Cl)$ (M = Th, U, R = Me, Et) the proton NMR spectra exhibit magnetically inequivalent alkyl functionalities.[81] High-temperature NMR studies result in an estimated ΔG^* of >23 kcal mol^{-1} for these rotation processes. Similar behavior is seen for $Cp_3U(\eta^2\text{-}CONEt_2)$,[40,83] $Cp_2U(NEt_2)(\eta^2\text{-}RNCNEt_2)$, and $Cp_2U(\eta^2\text{-}RNCNEt_2)_2$ (R = C_6H_{11}, xy).[82] In the carboxyphosphide $Cp^*HfCl_2(\eta^2\text{-}COPBu^t_2)$, rotation about the C_{acyl}–P bond is rapid on the NMR time scale at room temperature but slows down upon cooling.[86] At the coalescence temperature (−58 °C), ΔG^* is calculated to be 10.7 ± 0.1 kcal mol^{-1}.

V. Reactions of η^2-Acyl, η^2-Iminoacyl, and Related Ligands

Isolated molecules containing η^2-acyl, η^2-iminoacyl, or related ligands undergo a variety of interesting transformations and reactions. Furthermore, functionalities of this type have been proposed or implicated as reactive intermediates in a wide range of cabonylation reactions. In the case of the high-valent early d-block, lanthanide, and actinide metals a large part of this observed reactivity was rationalized by invoking the importance of resonance pictures for these ligands that imparted significant amounts of carbene character to the acyl carbon atoms.[34,70] A more recent view, based on theoretical work, points to the energy of the empty π^*_{CO} orbital of the η^2-acyl as being a critical factor.[1,2] The lowering in energy of this orbital on η^2-bonding results in a situation best described as "carbenium ion like". In the following sections the major reactivity patterns that have been observed are outlined as well as the results of any mechanistic studies.

A. Migratory Deinsertion

One of the most basic types of reaction that can be visualized for any η^2-acyl or η^2-iminoacyl ligand is deinsertion, with release of carbon monoxide or isocyanide. In early transition metal η^2-acyl complexes this behavior occurs in a number of group 4 metallocene derivatives.[12,79] In $Cp_2Hf(\eta^2\text{-}COR)(R)$ (R = Me, CH_2Ph) complexes, equilibrium constants and thermodynamic data can be obtained for the reversible CO insertion process. For R = Me, $\Delta H^* = -12.7 \pm 1.6$ kcal mol^{-1} and $\Delta S^* = -33.0 \pm 5.6$ cal K^{-1} mol^{-1}, while for R = CH_2Ph, $\Delta H^* = -11.5 \pm 0.2$ kcal mol^{-1} and $\Delta S^* = -28.7 \pm 0.6$ cal K^{-1} mol^{-1}.[8] Tilley has reported that $Cp_2Zr(\eta^2\text{-}COSiMe_3)(Cl)$ reacts with $LiOBu^t$, undergoing both substitution and decarbonylation to give $Cp_2Zr(SiMe_3)(OBu^t)$.[79]

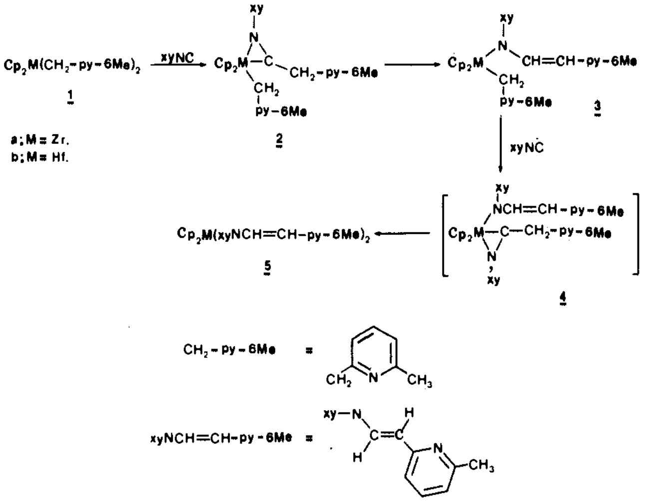
In contrast to the early transition metal systems, reversible carbonylation in actinide systems has been seen in η^2-acyl, η^2-formyl, and η^2-carbamoyl complexes.[37,40,72] The uranium complexes $Cp_3U(\eta^2\text{-}COR)$ (R = Me, Et, Pr^i, Bu^n, Bu^t) undergo decarbonylation at 60 °C.[40] A room temperature CO uptake–60 °C CO extrusion sequence could be carried out repeatedly. In $Cp^*_2Th(\eta^2\text{-}COH)(OR)$ (R = $HCBu^t_2$, Ar-2,6-Bu^t_2), Marks et al. found that the formyl/hydride ratio increases with decreasing temperature and increasing CO pressure.[72] Spectroscopic analysis of the mixtures gives the following thermodynamic data: for R = $CHBu^t_2$, $\Delta H = -4.5 \pm 0.9$ kcal mol^{-1} and $\Delta S = -11.7 \pm 4.3$ eu; for R = Ar-2,6-Bu^t_2, $\Delta H = -6.9 \pm 1.5$ kcal mol^{-1} and $\Delta S = -23.9 \pm 7.4$ eu. In the former systems, the rate constant (−45 °C) for the carbonylation reaction is 8050 s^{-1} M^{-1} ($\Delta H^* = 9.2 \pm 0.4$ kcal mol^{-1}).[37] The decarbonylation primary isotope effect was shown to be 4.1 (5) at −54 °C.

B. Bonding Mode and 1,2-Shifts

1. η^2 to η^1 Bonding Mode

The simplest transformation that might be classified as a rearrangement involves an $\eta^2 \rightarrow \eta^1$ conversion of the acyl/iminoacyl ligand, and this has been mentioned as it relates to fluxionality. The molecules $CpMo(CO)_2(\eta^2\text{-}MeCNR)$ (R = Me, Ph) readily add tetracyanoethylene, trimethyl phosphite, and trimethylphosphine in a process that converts the η^2-iminoacyl group to an η^1-iminoacyl group.[57] In a related rearrangement, Carmona et al. have reported the conversion of an η^2-acyl ligand to an η^1-acyl ligand with a stabilizing

SCHEME XIII



β-C–H metal interaction.[106] Girolami has recently shown that carbonylation of $Fe(\eta^2\text{-}COCH_2CMe_3)X(CO)(dippe)$ leads to the η^1-acyl $Fe(\eta^1\text{-}COCH_2CMe_3)X(CO)_2(dippe)$ (X = Cl, Br; dippe = $Pr^i_2CH_2CH_2PPr^i_2$).[69b]

2. 1,2-Shifts

Several rearrangements of η^2-acyl or η^2-iminoacyl complexes lead to enolate or vinylamide species via intramolecular 1,2-shift migration.[18,36,38,39,107,108] The thorium acyl complexes $Cp^*_2Th(Cl)(\eta^2\text{-}COCH_2Bu^t)$ and $Cp_3Th(\eta^2\text{-}COPr^i)$ undergo a 1,2-hydrogen atom migration to generate enolate complexes.[35,36,38,39] In the former case the reaction requires elevated temperatures (100 °C, 15 h) and gives exclusively a cis product (eq 16). The trans isomer can be made via reaction of the

$$Cp^*_2Th(Cl)(\eta^2\text{-}COCH_2Bu^t) \rightarrow Cp^*_2Th(Cl)(\textit{cis}\text{-}OCH{=}CHBu^t) \quad (16)$$

η^2-acyl with $[Cp^*_2ThH_2]_2$.[36] The latter reaction is catalytic in the thorium hydride reagent and is proposed to involve initial insertion of the acyl carbon into a Th–H bond, followed by β-hydride elimination. For the $Cp_3Th(\eta^2\text{-}COPr^i)$ compound the isomerization takes place at room temperature over several weeks.

In the case of η^2-iminoacyls, Beshouri et al. observed similar behavior for $Cp_2M(\eta^2\text{-}(xy)NCCH_2\text{-}py\text{-}6\text{-}Me)(CH_2\text{-}py\text{-}6\text{-}Me)$ (M = Zr, Hf) complexes, resulting in the smooth formation of *trans*-vinylamide products (Scheme XIII).[109] The rearrangement follows first-order kinetics at 28 °C, with $k = 12.8 \times 10^{-5}\ s^{-1}$ for Zr and $11.9 \times 10^{-5}\ s^{-1}$ for Hf. Further reaction with organic isocyanides results in formation of bis(vinylamide) complexes via a second insertion, 1,2-shift sequence (Scheme XIII).[109]

Another common type of rearrangement involves a 1,2-silyl shift. The complexes $Cp_3Th(\eta^2\text{-}COCH_2SiMe_3)$ and $Cp^*_2Th(Cl)(\eta^2\text{-}COCH_2SiMe_3)$ rearrange to give $Cp_3Th[OC(SiMe_3){=}CH_2]$ and $Cp^*_2Th(Cl)[OC(SiMe_3){=}CH_2]$, respectively.[39] Another example of silyl migration is seen in Andersen's work with actinide metallacycles.[110] Two recent reports show that zirconocene complexes exhibit similar behavior.[107,108] In one case, the oligomeric zirconaoxirane species $Cp_2Zr[OC({=}CH_2)SiMe_2CH_2]_n$ results when Cp = C_5H_5. However, when Cp = C_5Me_5, the cyclic dienolate product $Cp^*_2Zr[OC({=}CH_2)SiMe_2(CH_2{=})(CO)]$ is isolated.

C. Intramolecular Alkylation: Formation of η^2-Ketone and η^2-Imine Complexes

One common reaction of early transition metal alkyls is the production of ketones upon carbonylation. This type of reactivity has been seen in both mononuclear and dinuclear systems.[111] Hence carbonylation of the dialkyls $CpV(Me)_2(PMe_3)_2$[112] or Cp_2TiR_2 (R = CH_2Ph, Ph)[12,113,114] leads to lower valent vanadium and titanium complexes along with eliminated acetone, dibenzyl ketone, and benzophenone, respectively (eq 17). A logical

$$Cp_2TiR_2 + 3CO \rightarrow Cp_2Ti(CO)_2 + R_2CO \quad (17)$$

sequence for this reactivity involves initial formation of a mixed alkyl,acyl complex prior to a second alkyl transfer to generate the ketonic fragment. A mechanistic study by Erker et al. on the carbonylation of Cp_2ZrPh_2 indeed shows the formation first of the "O-outside", η^2-acyl $Cp_2Zr(\eta^2\text{-}PhCO)(Ph)$. Above −50 °C a rapid rearrangement to the "O-inside" isomer occurs and then, at +70 °C, a second migration of the remaining phenyl group produces an η^2-benzophenone complex (eq 18).[115,116] The complex was shown to exist

$$Cp_2ZrPh_2 + CO \rightarrow \tfrac{1}{2}[Cp_2Zr(\eta^2\text{-}Ph_2CO)]_2 \quad (18)$$

in a monomer/dimer equilibrium, the dimeric unit being structurally characterized.[115] The treatment of $CpTaMe_4$ with CO was studied by Schrock and Wood.[117] At 25 °C the compound was found to rapidly absorb 1 equiv of CO to produce $Cp^*Ta(\eta^2\text{-}Me_2CO)(Me)_2$ in good yield. Further reaction with CO produced a tantalum oxo product containing a trimethylenolate ligand (eq 19). Intramolecular coupling of the η^2-

$$Cp^*Ta(\eta^2\text{-}Me_2CO)(Me)_2 + CO \rightarrow [Cp^*Ta(O)(OCMe{=}CMe_2)(Me)] \quad (19)$$

acetone group with an intermediate η^2-acyl followed by fragmentation was proposed as a possible pathway.[117] A similar cleavage of CO by the bis(alkyls) $[(Me_3Si)_2N]_2ZrMe_2$ was observed by Andersen et al.[118] However, whether an intermediate η^2-acetone complex is formed was not discussed.

A double aryl migration to CO was observed by Floriani et al. on carbonylation of $(\eta^8\text{-}C_8H_8)Zr(mes)_2$ (mes = 2,4,6-trimethylphenyl) to produce a dimeric η^2-ketone compound (eq 20).[119]

$$(\eta^8\text{-}C_8H_8)Zr(mes)_2 + CO \rightarrow \tfrac{1}{2}[(\eta^8\text{-}C_8H_8)Zr(\eta^2\text{-}(mes)_2CO)]_2 \quad (20)$$

mes = 2,4,6-trimethylphenyl

In a detailed mechanistic study, Grubbs et al. have demonstrated the ability of organoaluminum reagents to induce the second alkyl transfer in $Cp_2Zr(\eta^2\text{-acyl})(alkyl)$ substrates.[120] A number of aluminum-stabilized symmetric as well as asymmetric η^2-ketone complexes were obtained by this method (eq 21).

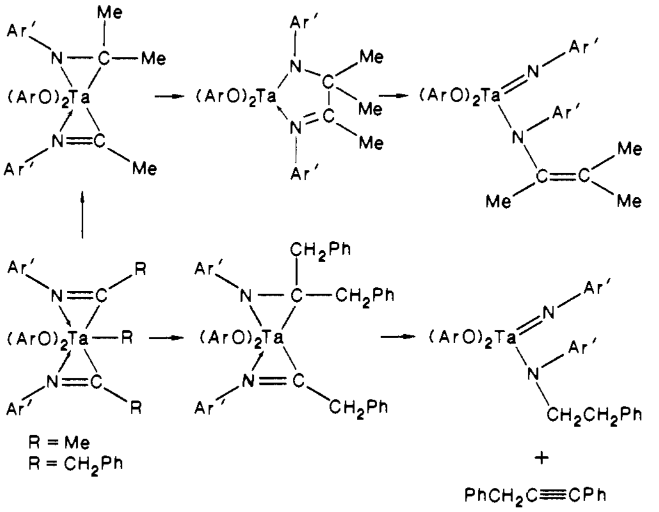
$$Cp_2Zr(Cl)(\eta^2\text{-}COR) + AlR'_3 \rightarrow [Cp_2Zr(\mu\text{-}\eta^2\text{-}RR'CO)(\mu\text{-}Cl)AlR'_2] \quad (21)$$

R = CH_3, C_2H_5, $(CH_2)_2CMe_3$, c-C_6H_{11}; R′ = CH_3

R = $(CH_2)_2CMe_3$; R′ = C_2H_5

The multiple alkylation of organic isocyanides to produce η^2-imine functions is also common. Again

SCHEME XIV



Ar = 2,6-dimethylphenyl; Ar' = 2,6-dimethyl- or 2,6-diisopropylphenyl

pathways involving intermediate η^2-iminoacyl complexes are well justified. Early work by Wilkinson et al. on the reaction of WMe_6 with Bu^{t}NC clearly demonstrated the range of different functionalities that could be obtained at early transition metal centers by this route. The structurally characterized product contains not only an η^2-imine ligand but also vinylamido as well as imido groups (eq 22).[121,122]

$$WMe_6 + 3Bu^tNC \rightarrow W(NBu^t)(Bu^tNCMe{=}CMe_2)(Me)(\eta^2\text{-}Me_2CNBu^t) \quad (22)$$

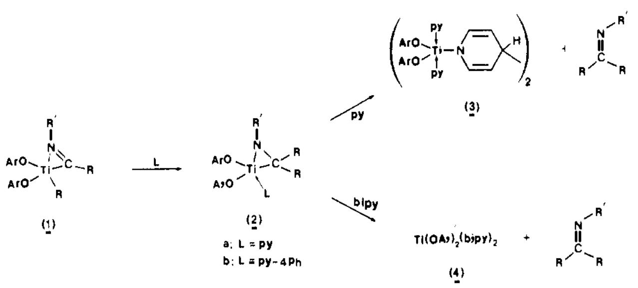
The tris(alkyls) $Ta(OAr)_2R_3$ (R = CH_3, CH_2Ph; OAr = 2,6-dimethylphenoxide) react with 2 equiv of aryl isocyanides to generate bis(η^2-iminoacyl) derivatives.[20] In the case R = CH_3, mild thermolysis results in the formation of a mixed amido,imido complex of tantalum (Scheme XIV).[52] The reaction is believed to proceed via initial formation of a mixed η^2-imine, η^2-iminoacyl intermediate that rapidly couples and fragments to generate the observed product.[52] Strong support for this comes from the reaction of $Ta(OAr)_2Ph_3$ with Bu^{t}NC, which produces a stable, mixed η^2-imine,η^2-iminoacyl compound directly (eq 10).[54] Thermolysis then leads to a mixed imido,vinylamido product, which has been structurally characterized.[54]

The mono(η^2-iminoacyl) derivatives of titanium of stoichiometry $Ti(OAr)_2(\eta^2\text{-}R'NCR)(R)$ undergo a second, donor ligand induced alkyl migration to generate η^2-imine complexes (Scheme XV).[123,124] In one case the product has been structurally characterized and clearly shows the η^2-bonding of the imine fragment with bonding parameters consistent with the presence of an azametallacyclopropane ring.[123] Reaction with further equivalents of donor ligands actually leads to reductive elimination of free imine and the formation of lower valent titanium complexes (Scheme XV).

D. Formation of Enediolates, Enediamides, and Enamidolates

One of the most characteristic of reactions for early d-block, lanthanide, and actinide metal η^2-acyls, formyls, and iminoacyls is their inter- or intramolecular coupling to produce enediolate or related fragments.

SCHEME XV



This type of reactivity was first documented by Bercaw et al., who showed that further, more forceful carbonylation of the η^2-acyl $Cp^*_2Zr(\eta^2\text{-}MeCO)(Me)$ led to a monomeric enediolate complex (eq 23).[17,125] Similar

$$Cp^*_2Zr(\eta^2\text{-}COMe)(Me) + CO \rightarrow Cp^*_2Zr(OCMe{=}CMeO) \quad (23)$$

reactivity was also shown by Marks et al. for carbonylation of the organoactinide complex $Cp^*_2ThMe_2$, only this time the product was found to be dimeric, linked by two *cis*-enediolate bridges (eq 24).[101] The bis(alkyl)

$$Cp^*_2Th(Me)_2 + 2CO \rightarrow \tfrac{1}{2}[Cp^*_2Th(cis\text{-}OCMe{=}CMeO)_2ThCp^*_2] \quad (24)$$

$Cp^*_2Th(CH_2SiMe_3)_2$ was shown, however, to produce a monomeric, chelating enediolate product.[101] Later work involving labeling studies showed that all enediolate fragments were formed at a single metal center, presumably by rapid intramolecular coupling in a bis(η^2-acyl) intermediate.[127]

Treatment of the hafnium metallacycle $Cp_2Hf(CH_2CH_2CH_2)$ with CO was found to result in formation of a dinuclear product containing an enediolate ligand, the olefinic part also being contained in a cyclopentene ring.[128] Furthermore, the molecule was also shown to contain an η^2-cyclobutanone fragment.[128] The intermediacy of η^2-acyl functions was postulated for the formation of both these groups.

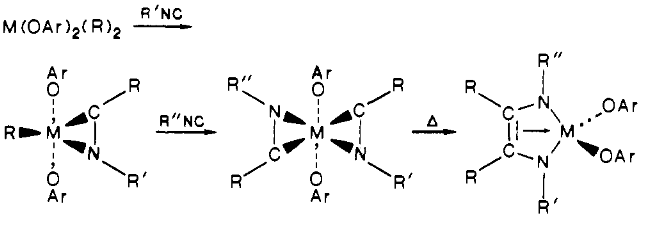
The somewhat related metallacycle compound $Cp^*_2Zr(CH_2SiMe_2CH_2)$ also forms an enediolate product as well as the rearrangement products alluded to earlier.[107]

The reaction of early transition metal hydrides with CO can sometimes lead to the formation of enediolates. For the lanthanide system $[Cp^*_2SmH]_2$, Evans et al. have shown that carbonylation in the presence Ph_3PO forms a dimeric, *cis*-enediolate complex (eq 25).[129] Over a period of days isomerization to the *trans*-enediolate takes place.

$$[Cp^*_2SmH]_2 + 2CO \rightarrow [Cp^*_2Sm(cis\text{-}OCH{=}CHO)SmCp^*_2] \quad (25)$$

The discrete η^2-formyl compounds $Cp^*_2Th(OR)(\eta^2\text{-}HCO)$ isolated by Marks et al. also undergo apparent intermolecular coupling to produce enediolate dimers.[72,130] However, a careful mechanistic study showed that in fact the reaction proceeds via initial attack of a thorium hydride on an η^2-formyl group to produce an intermediate bridging formaldehyde complex. Subsequent carbonylation and rearrangement then generates the *cis*-enediolate bridge.[130] Interception of the formaldehyde intermediate by hydrogenation led to the formation of a methoxide group.

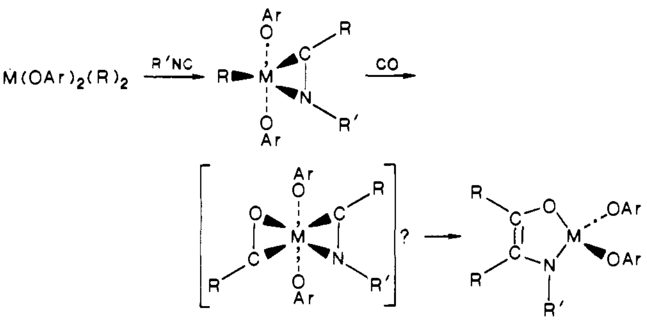
SCHEME XVI



II

compd	M	OAr	R	R′	R″
IIa	Ti	OAr-2,6-$\mathrm{Pr^i_2}$	$\mathrm{CH_2Ph}$	xy	xy
IIb	Ti	OAr-2,6-$\mathrm{Pr^i_2}$	$\mathrm{CH_2Ph}$	Ph	$\mathrm{Bu^t}$
IIc	Ti	OAr-2,6-$\mathrm{Pr^i_2}$	$\mathrm{CH_2Ph}$	xy	$\mathrm{Bu^t}$
IId	Zr	OAr-2,6-$\mathrm{Bu^t}$	$\mathrm{CH_3}$	xy	xy
IIe	Zr	OAr-2,6-$\mathrm{Bu^t_2}$	$\mathrm{CH_2Ph}$	Ph	Ph
IIf	Zr	OAr-2,6-$\mathrm{Bu^t_2}$	$\mathrm{CH_3}$	Ph	Ph
IIg	Hf	OAr-2,6-$\mathrm{Bu^t_2}$	$\mathrm{CH_3}$	Ph	Ph

SCHEME XVII



I

Ia, M = Ti; OAr = OAr-2,6-$\mathrm{Pr^i_2}$; R = $\mathrm{CH_2Ph}$; R′ = $\mathrm{Bu^t}$
Ib, M = Zr; OAr = OAr-2,6-$\mathrm{Bu^t_2}$; R = $\mathrm{CH_2Ph}$; R′ = xy

The intramolecular coupling of two η^2-iminoacyl groups at both group 4 and group 5 metal centers to produce chelating enediamide ligands has been demonstrated (Scheme XVI).[131] In these cases the bis(η^2-iminoacyl) precursors supported by aryl oxide coligation are sufficiently stable to be isolated. Mild thermolysis in hydrocarbon solvents induces the carbon–carbon double-bond-forming process to take place. A series of kinetic measurements as well as crossover experiments show the reactions to be first-order, intramolecular processes. A number of the product molecules have been structurally characterized. An interesting feature of the group 4 metal derivatives is a puckering of the five-membered chelate ring, which results in the olefinic carbon atoms being brought closer to the metal center, possibly to aid in relieving its electron deficiency. In the case of tantalum, the endiamido ring is planar.[52,54,131]

Attempts to prepare a mixed η^2-acyl, η^2-iminoacyl compound by carbonylation of mono(η^2-iminoacyl),alkyl substrates failed, resulting in the formation of enamidolate complexes (Scheme XVII).[131,132] The presumed intermediate mixed acyl,iminoacyl rapidly undergoes carbon–carbon bond formation even at room temperature.

Theoretical studies by Hoffmann et al. on the double carbonylation of $\mathrm{Cp^*_2MR_2}$ (M = Th, U) substrates to produce enediolate ligands points to a bis(η^2-acyl) intermediate.[127] However, the initially expected coupling pathway in which the acyl groups remain coplanar within the equatorial girdle was found to be a symmetry-forbidden, high-energy process. Instead, initial kinking of the groups out of this plane prior to carbon–carbon bond formation was found to be the lowest energy pathway.[127] A critical parameter in controlling the activation barrier for reaction was found to be the energy of the π^*_{CO} orbital. Similarly, the lower reactivity of η^2-iminoacyl groups toward these coupling reactions compared to their oxygen counterparts may be ascribed to the higher energy of the π^*_{CN} orbital.[133] A detailed kinetic study of the intramolecular coupling of η^2-iminoacyl groups at group 4 metal centers showed a dependence of the rate of coupling not only on the metal (Ti > Zr > Hf) but also a dependence on the electronic nature of the nitrogen substituent.[133] In particular, use was made of various meta- and para-substituted phenyl groups attached to the nitrogen of the η^2-iminoacyl group. It was found that electron-withdrawing substituents enhanced the rate of reaction while electron-donating groups caused a retardation (Figure 9).[133] Again this observation is consistent with the idea that the energy of the π^*_{CO} or π^*_{CN} orbitals are important in deciding the barrier to intramolecular coupling.

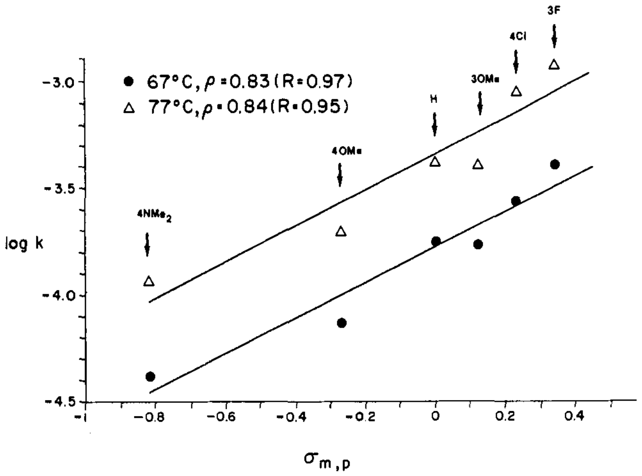


Figure 9. Plot of log k vs $\sigma_{m,p}$ for the intramolecular coupling of the η^2-iminoacyl groups in $\mathrm{Zr(OAr\text{-}2,6\text{-}Bu^t_2)_2(\eta^2\text{-}Ar^*NCMe)_2}$ (Ar* = various substituted aryls).

A somewhat related reaction reported by Curtis et al. involves the intramolecular coupling of a tantalum η^2-iminoacyl with an alkyne ligand to generate an azametallacyclopentadiene ring.[59] The metallacycle was again found to be puckered and theoretical calculations using the EHMO method suggested the folding occurred to relieve unfavorable electronic interactions present for a planar ring.

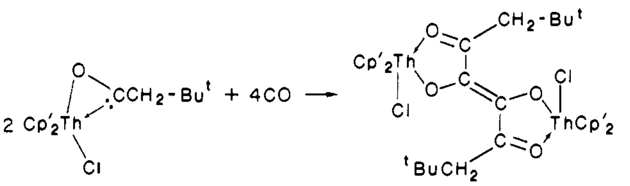
E. Further Reactions with CO or RNC

Numerous high-valent early transition metal η^2-acyl ligands have been shown to be able to react with further equivalents of CO or RNC. The immediate products of these reactions are ketene or ketenimine groups, which may or may not be isolable. The fact that such ketene species are formed in these reactions is sometimes taken as a strong indication of the carbene-like nature of η^2-acyl carbon (eq 26). The ketene groups

$$\mathrm{L_nM(\eta^2\text{-}COR) + CO \rightarrow L_nM(OCR{=}C{=}O)} \qquad (26)$$

formed by reaction with CO tend to be only transitory intermediates that either dimerize or can be trapped.

SCHEME XVIII



Hence carbonylation of $Cp^*_2Th(\eta^2\text{-}COCH_2Bu^t)Cl$[36,38,108] or $Cp_2Lu(\eta^2\text{-}COBu^t)$[44] leads to dimeric compounds containing enedionediolate linkages (Scheme XVIII). Both reactions were proposed to proceed via initial formation of ketene complexes that subsequently dimerized to the final product. In the case of the thorium compound the carbonylation was found to be second order.[95] The intermediate ketene could be trapped by added phosphine to generate ylide compounds.[95,108]

It has been found that ketenimine complexes formed by reaction of alkyl isocyanides with η^2-acyl groups are much more stable than their oxygen counterparts. Hence treatment of $Cp^*_2Th(\eta^2\text{-}COCH_2Bu^t)(Cl)$ with RCN yields insoluble ketenimine complexes (eq 27),[95]

$$Cp^*_2Th(Cl)(\eta^2\text{-}COCH_2Bu^t) + RNC \rightarrow Cp^*_2Th(Cl)[OC(CH_2Bu^t){=}C{=}NR] \quad (27)$$

$$R = \text{2,6-dimethylphenyl}$$

one of which has been structurally characterized. Similarly, the η^2-silaacyl $Cp_2Zr(\eta^2\text{-}COSiMe_3)(Cl)$ reacts with 2,6-dimethylphenyl isocyanide to produce a stable ketenimine.[79]

The carbonylation of the tantalum silyl compound $Cp^*Ta(SiMe_3)Cl_3$ in the presence of diethyl ether yields a chelating α-keto alkoxide ligand thought to possibly be formed by ether attack on an intermediate ketene compound.[135]

F. Adduct Formation with Lewis Bases

Theoretical calculations that point to the electrophilic nature of the carbon atoms in η^2-acyls as being pivotal to their reactivity is given support in the fact that facile adduct formation can take place at this carbon. Hence addition of pyridine to solutions of the silaacyl complex $Cp^*Ta(\eta^2\text{-}COSiMe_3)Cl_3$ is found to generate an adduct.[136] Structural studies clearly show the now tetrahedral acyl carbon atom (eq 28). Similar adducts were also isolated with trialkylphosphines and trialkyl phosphites.[136]

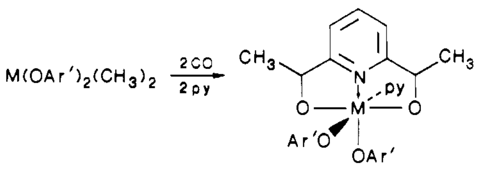
$$Cp^*TaCl_3(\eta^2\text{-}COSiMe_3) + py \rightarrow Cp^*TaCl_3[\eta^2\text{-}OC(py)SiMe_3] \quad (28)$$

G. "Insertion" into CH Bonds

Evans et al. have reported that treatment of $Cp^*_2Sm(thf)_2$ with diphenylacetylene followed by CO (90 psi) results in the formation of a dihydroxyindenoindene unit.[137] The reaction is believed to proceed via formation of an intermediate, dinuclear η^2-acyl complex that subsequently rearranges to the product by insertion of the acyl carbon into the ortho-CH bond of an aryl group.

Early d-block η^2-acyls have also been shown to be able to insert into the ortho-CH bonds of pyridine ligands to produce α-substituted pyridine–methoxide chelates. Hence carbonylation of the dialkyls $(OAr)_2MR_2$ (OAr = 2,6-di-*tert*-butylphenoxide; R = CH_3, CH_2Ph) in the presence of pyridine is found to yield α,α-disubstituted pyridinedimethoxide groups in high yield (Scheme XIX).[138] The lack of an isotopic preference when using a 50/50 excess of C_5H_5N and C_5D_5N was interpreted in terms of a pathway involving nucleophilic attack of the acyl carbon on the heterocycle ring followed by a fast 1,2-hydrogen shift to generate the product.[138]

SCHEME XIX



1, M = Zr
2, M = Hf

Tilley et al. have also shown that early transition metal η^2-silaacyls can attack pyridine to generate α-silylpyridinemethoxide groups.[139] Carbonylation of $Cp^*HfCl_2[Si(SiMe_3)_3]$ in the presence of pyridine yields the pyridinemethoxide in high yield (eq 29). A

$$Cp^*HfCl_2(tts) + CO + C_5H_5N \rightarrow Cp^*HfCl_2[OCH(tts)C_5H_4N] \quad (29)$$

$$tts = Si(SiMe_3)_3$$

mechanistic study was also found to be consistent with a nucleophilic attack pathway.[139] Addition of pyridine to the phosphine adduct $Cp^*TaCl_3[\eta^2\text{-}OC(SiMe_3)(PR_3)]$ was found not to lead to any simple pyridine adduct, but to $Cp^*TaCl_3[NC_5H_4CH(SiMe_3)O]$.[139]

H. Reaction with Hydridic Reagents

The reaction of high-valent early d-block, lanthanide, and actinide hydrides with CO or RNC typically can lead to aldehyde, alkoxide, or amido functionalities.[8] These reactions are typically envisioned to proceed via initial formation of an η^2-formyl or η^2-iminoformyl intermediates, which then undergo further reaction either inter- or intramolecularly with other metal–hydride bonds. Extensive mechanistic studies have been performed on the carbonylation of the hydride compound Cp^*ZrH_2, which leads to differing products depending on the reaction conditions.[17,70] In the absence of added H_2, the major product is a *trans*-enediolate dimer. However, added H_2 results in the formation of a methoxide ligand. These results can be explained in terms of an intermediate formaldehyde-bridged dimer, $[Cp^*_2Zr(H)(OCH_2)Zr(H)Cp^*_2]$ formed by attack of a $Cp^*_2ZrH_2$ molecule on an η^2-formyl intermediate.[17,70] Similarly, the hydrides $Cp^*_2Th(H)(OR)$ produce a *cis*-enediolate or carbonylation, and kinetic/mechanistic studies again demonstrate the intermediacy of a highly reactive formaldehyde-bridged compound (eq 30).[130] In

$$Cp^*_2Th(\eta^2\text{-}COH)(OR) + Cp^*_2Th(H)(OR) \rightarrow [Cp^*_2Th(OR)(\mu\text{-}OCH_2)ThCp^*_2(OR)] \quad (30)$$

the case of the compound $[Cp_2Zr(H)Cl]_n$, Floriani has actually shown the formation of an isolable bridging formaldehyde (oxymethylene) dimer (eq 31).[140] Im-

$$[Cp_2Zr(H)Cl]_n + CO \rightarrow [Cp_2ZrCl(\mu\text{-}OCH_2)ZrClCp_2] \quad (31)$$

portant model studies for these reactions comes from the reaction of isolable η^2-acyls with reducing-metal hydrides to generate either isolable or intermediate bridging aldehyde linkages (eq 32). Early work by

$$Cp_2Zr(\eta^2\text{-}COR)(X) + L_nM\text{-}H \rightarrow [Cp_2Zr(X)(OCHR)ML_n] \quad (32)$$

Schwartz on the carbonylation of $Cp_2Zr(H)R$ showed that the products obtained either before or after hydrolysis could be adequately explained as arising via an intermediate with the linkage $Zr^{IV}\text{-}OCRH\text{-}Zr^{IV}$ formed by intermolecular attack of a Zr–H bond on an η^2-RCO unit.[141] A structurally characterizable complex containing just such a linkage has been obtained by Erker et al. for the reaction of the η^2-acyls $Cp_2Zr(\eta^2\text{-}RCO)(R)$ with the polymeric hydride $[Cp_2ZrH_2]_x$.[142]

The thorium hydride $[Cp^*{}_2ThH_2]_2$ has been shown to effect the catalytic hydrogenation of the η^2-acyl compounds $Cp^*{}_2M(\eta^2\text{-}RCO)Cl$ (M = Th, U) under less than 1 atm of H_2. Mechanistic studies indicate the intermediacy of a bridging aldehyde complex of the type $Cp^*{}_2Th(U)[OCRH](H)ThCp^*{}_2$, which undergoes rapid hydrogenolysis to regenerate $(Cp^*{}_2ThH_2)_2$ and the alkoxide $Cp^*{}_2Th(OCH_2R)Cl$.[143]

Extensive studies on the formation of heterobimetallic complexes containing bridging aldehyde ligands have been carried out. Typically η^2-acyl substrates of the type $Cp_2Zr(\eta^2\text{-}RCO)(X)$ are treated with metal hydrides L_nMH.[144] A detailed survey of the reaction by Caulton and Marsella has shown that the fate of the initial bimetallic compounds of the type $Cp_2Zr(X)[OCH(R)]ML_n$ is highly dependent on the ML_n group. For Cp_2MoH_2 as the hydride source, "molybdenocene" and the alkoxide $Cp_2Zr(OCH_2R)(X)$ are generated. With Cp_2WH_2 complete C–O bond scission is seen to generate the carbene complex $Cp_2W{=}CHR$ along with oxo zirconium compounds.[144,145] A stable, structurally characterized intermediate was obtained with Cp_2ReH, however.[8,146]

The tantalum dihydride $(silox)_3TaH_2$ has been shown by Wolczanski to react with CO to form a discrete η^2-formaldehyde complex.[147]

I. Reaction with Protic Reagents

The simple cleavage of the metal–η^2-acyl bond can usually be effected by acidic reagents to produce aldehydes.[63,79] Recent work by Tilley et al. has shown that this method offers a good route to the silaaldehydes, via protonation of intermediate η^2-silaacyl complexes (eq 33).[148] Treatment of η^2-iminoacyls with acid has also been shown to lead to aldehydes.[111a]

$$CpCp^*ZrCl[\eta^2\text{-}CO(tts)] + HCl \rightarrow CpCp^*ZrCl_2 + (tts)CHO \quad (33)$$

$$tts = Si(SiMe_3)_3$$

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