Formation of η^2-Iminoacyls, η^3-Azaallyls, and Heterometallacycles during the Rearrangements of Methyl Complexes of Molybdenum and Tungsten Containing Isocyanide Ligands

P. James Daff,[†] Angeles Monge,[‡] Pilar Palma,[†] Manuel L. Poveda,*[,†] Caridad Ruiz,[‡] Pedro Valerga,[§] and Ernesto Carmona*[,†]

Departamento de Química Inorgánica-Instituto de Investigaciones Químicas, Universidad de Sevilla-Consejo Superior de Investigaciones Científicas, C/ Americo Vespucio s/n, Isla de la Cartuja, 41092 Sevilla, Spain, Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Campus de Cantoblanco, 28049 Madrid, Spain, and Departamento de Ciencia de Materiales, Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Apdo 40, 11510 Puerto Real, Cádiz, Spain

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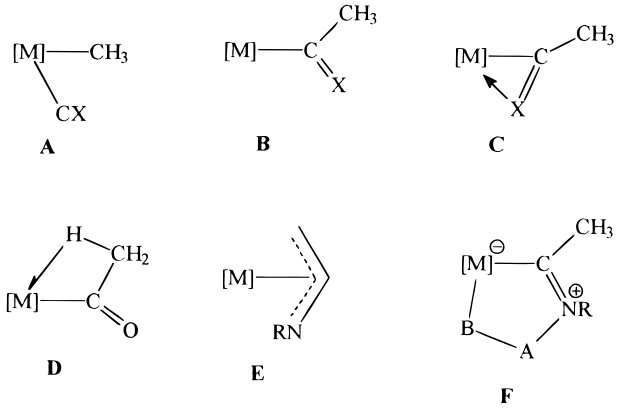
The metalate salts $Y^+[Cp'M(CO)_2(CNR)]^-$ (Y = Na, K; M = Mo, W; CNR = alkylisocyanide), in the presence of the soft electrophile MeI, experience alkylation at the metal center to afford methyl complexes of composition $Cp'MMe(CO)_2(CNR)$. The kinetic stability of these alkyls toward rearrangement to the η^2-iminoacyls $Cp'M(\eta^2\text{-}C(=NR)Me)(CO)_2$ or the η^3-1-azaallyls $Cp'M(\eta^3\text{-}CH_2C(H)NR)(CO)_2$ has been found to depend markedly upon the nature of the metal, the isocyanide R substituent, and the solvent used. With respect to the latter, solvents with efficient Lewis basic capabilities (*e.g.*, pyridine or acetonitrile) favor η^2-iminoacyl formation while those which are poor donors (benzene, diethyl ether) preferentially generate the η^3-azaallyls. The use of acetone as the solvent in reactions involving the Me−W−CNR complexes has allowed the isolation of metallacyclic structures of composition $Cp'W(\eta^2(C,O)\text{-}C(Me)=N(R)C(Me)_2O)(CO)_2$, formally as the result of a [3 + 2] cycloaddition of a $W-\eta^1\text{-}C(=NR)Me$ residue to a molecule of acetone. Two of the newly reported complexes, namely the η^3-1-azaallyl $CpMo(\eta^3\text{-}CH_2CHN\text{-}t\text{-}Bu)(CO)_2$ (**1az**) and the heterometallacycle $CpW(\eta^2\text{-}(C,O)\text{-}C(Me)=N(Me)C(Me)_2O)(CO)_2$ (**9cad**) have been structurally characterized by X-ray crystallography.

Introduction

The involvement of transition metal acyls in many valuable stoichiometric and catalytic reactions of CO has motivated a number of synthetic, mechanistic, and reactivity studies of these complexes and of the associated transformation by which they are formed, namely the migratory insertion of CO into transition-metal−carbon bonds.[1] Organic isocyanides, RNC, are isoelectronic with CO and exhibit similar bonding capabilities, although they are regarded as somewhat better σ-donors and less efficient π-acceptors.[2] Their insertion into M−C bonds is also a commonly observed transformation,[1b,d,3] which has often been investigated in modeling studies of the commercially more important CO insertion reaction.

There are many similarities between the two processes, but important differences also exist. Both acyl and iminoacyl (or imidoyl) ligands can be monodentate or bidentate (structures **B** and **C**, respectively, illustrated for a methyl derivative **A**; X = O, NR),



although the latter bonding mode is more often encountered in iminoacyls than in acyls. Polyinsertions are only common for iminoacyls,[4] while deinsertions are facile for acyls and infrequent for iminoacyls.[1,5] The

[†] Universidad de Sevilla-CSIC.
[‡] Instituto de Ciencia de Materiales de Madrid.
[§] Universidad de Cádiz.
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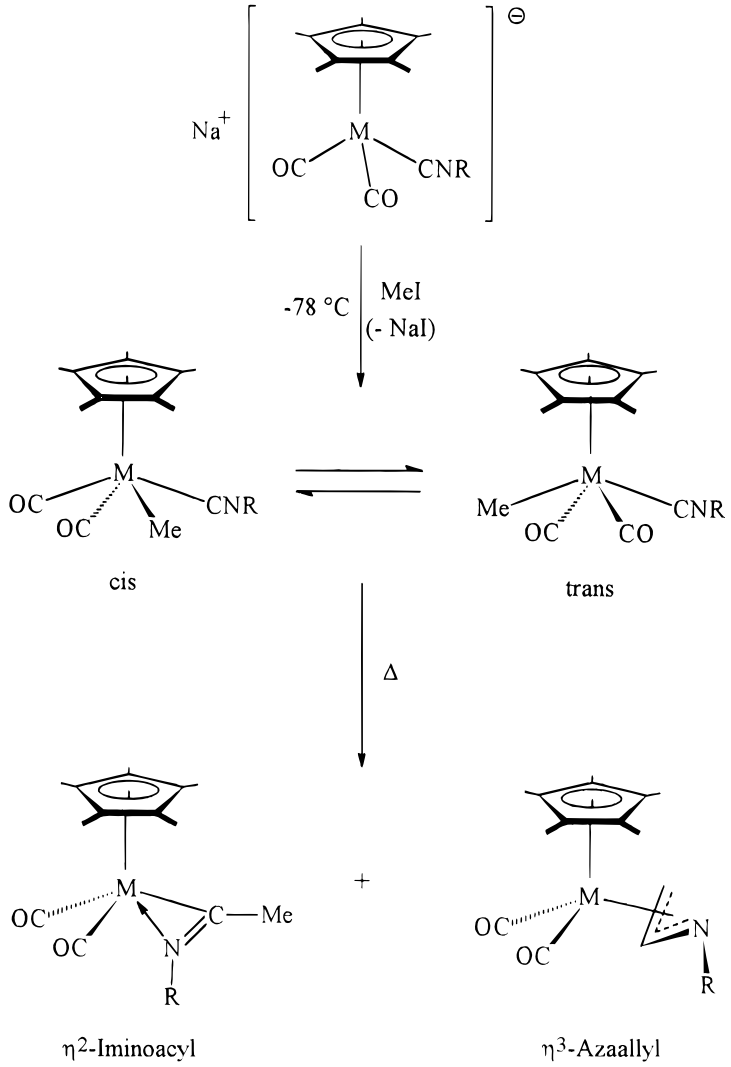
Scheme 1



Cp'	M	R	
η^5-C_5H_5	Mo	*t*-Bu	**1**
η^5-C_5H_4Me	Mo	*t*-Bu	**2**
η^5-C_5Me_5	Mo	*t*-Bu	**3**
η^5-C_5Me_5	Mo	*i*-Pr	**4**
η^5-C_5H_5	W	*t*-Bu	**5**
η^5-C_5Me_5	W	*t*-Bu	**6**
η^5-C_5H_5	W	*i*-Pr	**7**
η^5-C_5Me_5	W	*i*-Pr	**8**
η^5-C_5H_5	W	Me	**9**
η^5-C_5Me_5	W	Et	**10**

agostic acyl structure **D** has been ascertained in a few instances[6] but is conspicuously absent in iminoacyl chemistry. In recent years, independent and almost simultaneous work from Filippou and co-workers[7] and from ourselves[8] has shown that η^3-1-azaallyl structures of type **E** can also be formed in reactions involving the coupling of CNR and M−C bonds. Finally, although always with reference to complexes that involve only one metal center and one molecule of CNR, metallacyclic structures of type **F** have been detected when isocyanide insertion takes place in polar solvents like acetone or acetonitrile (A−B = $-C(Me_2)O-$ or $-C(Me)N-$).[2,9]

Pioneer work by Adams and co-workers on Mo−iminoacyl chemistry showed that the reaction of the metalate $[CpMo(CO)_2(CNR)]^-$ (R = Me, Ph) with MeI gives η^2-iminoacyls $CpMo(\eta^2\text{-}C(=NR)Me)(CO)_2$, which in the presence of donor ligands undergo an η^2 to η^1 rearrangement.[10] Subsequent work from Winter et al. on related systems gave similar results.[11] The chemistry we wish to describe here stems from the unexpected observation that the room temperature reaction of $[CpMo(CO)_2(CN\text{-}t\text{-}Bu)]^-$ (*i.e.*, the CN-*t*-Bu analogue of Adams' starting material) with MeI in THF yields a mixture of *cis*- and *trans*-$CpMoMe(CO)_2(CN\text{-}t\text{-}Bu)$, which only at higher temperatures in the same solvent transforms into the expected η^2-iminoacyl, $CpMo(\eta^2\text{-}C(=N\text{-}t\text{-}Bu)Me)(CO)_2$. However, under these conditions, the η^3-1-azaallyl isomer $CpMo(\eta^3\text{-}CH_2CHN\text{-}t\text{-}Bu)(CO)_2$ is also formed. We present full details[8] of this work that encompasses the description of a variety of complexes with structures of the types **A**, **C**, **E** and **F**.

Results and Discussion

Synthesis and Characterization of Isomeric Methyl−M−Isocyanide, η^2-Iminoacyl, and η^3-Azaallyl Complexes. Scheme 1 is a pictorial representation of the synthetic procedure used for the preparation of the methyl−M−isocyanide (suffix **al**), η^2-iminoacyl (**im**),

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and η^3-1-azaallyl (**az**) derivatives described in this work. Arab numerals are employed to denote the different combinations of the cyclopentadienyl ligand (C_5H_5, C_5H_4Me, and C_5Me_5), metal (Mo or W), and isocyanide, CNR (R = Me, Et, *i*-Pr, and *t*-Bu), within the above classes of compounds.

As described previously,[7,8,10,11] the low temperature addition of MeI to tetrahydrofuran (THF) solutions of the metalates $[Cp'M(CO)_2(CNR)]^-Na^+$ generates the methyl complexes $Cp'MMe(CO)_2(CNR)$ in essentially quantitative yields. In those examples for which M = Mo, only the derivatives bearing the sterically encumbered *tert*-butyl substituent display sufficient kinetic stability to allow isolation as crystalline solids (thus, complex **4al** has only been studied in solution at low temperature). This is in contrast to the analogous tungsten containing compounds, all of which are isolable at room temperature as yellow, moderately air-sensitive solids. Of these last-mentioned species, complexes **9al** and **10al** have been reported previously by other workers,[10a,11,7a] although the data reported by Adams and Chodosh for **9al**[10a] actually pertain to the isomeric η^2-iminoacyl $CpW(\eta^2\text{-}C(=NMe)Me)(CO)_2$ and not the parent methyl as claimed. We, thus, include details for the preparation and full characterization of **9al** herein.

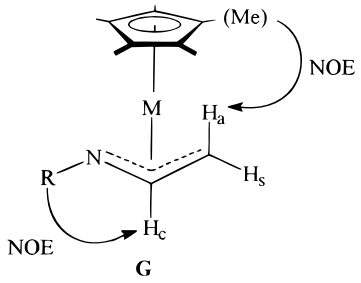
The isolated M−Me (**1al**−**3al** and **5al**−**10al**) derivatives exist in solution as equilibrium mixtures of cis and trans isomers, as evidenced by their NMR spectra. As in most cases, the ratio of cis:trans isomers is close to unity, specific assignments of ^1H and ^{13}C resonances to individual species were not attempted (see Experimental Section). Their predominant decomposition pathway in the absence of air and moisture involves the intramolecular migration of the metal-bound Me group to the isocyanide ligand, followed by coordination of N to the metal to generate the isomeric η^2-iminoacyl. This is a clean transformation that may be monitored conveniently in solution by spectroscopic techniques, the terminal isocyanide stretching mode which occurs in the IR spectrum in the region of 2100 cm^{-1} diminishes in intensity as the iminoacyl C−N stretch, at approximately 1700 cm^{-1}, increases. In the ^1H NMR spectrum, the high-field methyl singlets are replaced by a characteristic iminoacyl N-methyl resonance in the range 2.0−2.5 ppm. As only the cis isomer would be expected to give rise to the migratory insertion reaction, the observation that both cis and trans isomers are consumed concomitantly would indicate that they exist in rapid equilibrium at thermal transformation temperatures. The η^2-iminoacyls are red crystalline solids, soluble in all common organic solvents. They display moderate sensitivity to air and moisture, in the presence of which they decompose to the corresponding amides, HC(O)NHR, and other unidentified metal containing materials. For these complexes, the most distinctive spectroscopic features are those concerning the M−η^2-C(=NR)Me linkage. All the compounds of this type described here are characterized by a ν_{CN} frequency in the proximity of 1700 cm^{-1} and by a ^{13}C resonance for the metal-bound iminoacyl carbon in the approximate range of 185−200 ppm. These results compare well with related values for other η^2-iminoacyls which have been structurally characterized[1b,10] and, therefore, provide strong support for the bidentate bonding mode of the iminoacyl functionality in the compounds described in this work.[12]

In contrast to prior reports concerning the generation of compounds of this general type, we[8] and others[7] have independently observed the formation of the hitherto undetected isomeric η^3-1-azaallyls, $Cp'M(\eta^3\text{-}CH_2CHNR)(CO)_2$ (Scheme 1). Interestingly, the proportion of the η^3-azaallyl generated during the thermolysis of the methyl−M−isocyanide species was observed, qualitatively, to display a dependency upon the kinetic stability of the parent Me−M−CNR derivative, which increases considerably for sterically demanding R groups and when W is employed in place of Mo. Perhaps more noteworthy was the verification (to be discussed below in detail) that the molar ratio of the products (η^2-iminoacyl:η^3-1-azaallyl) shows a remarkable dependence upon the donor properties of the solvent employed during thermolysis. In all these cases, the transformation is under kinetic control, as no iminoacyl−azaallyl interconversion is detectable under the conditions used for their generation.

At the outset of this work, information on η^3-1-azaallyl complexes of the transition metals was very scarce.[13a,b] Subsequent reports have described other transition metal η^3-azaallyls;[7,13,14] additionally, some alkali metal derivatives[15a−c] and a molybdenum complex of a protonated azaallyl ligand have also been reported.[15d] In recent years, Filippou et al. have described some reactivity studies of the coordinated azallyl fragment.[16]

The η^3-1-azaallyls have been shown to be the overall thermodynamic products of the thermolysis of the Me−M−CNR derivatives, several *N*-ethyl η^2-iminoacyls having been isomerized to the corresponding η^3-azaallyls over a period of 24 h in refluxing toluene.[7] However, attempts at effecting this transformation with the bulkier *N*-*tert*-butyl iminoacyls in these laboratories met with limited success, higher temperatures proved necessary and decomposition was significant. The η^3-1-azaallyls are yellow-brown crystalline solids, stable in air for several days. They undergo protonation in acidic media to give water-soluble η^3-azaallyl salts of proposed composition $[Cp'M(\eta^3\text{-}CH_2CHN(H)R)(CO)_2]^+Y^-$ (*e.g.*, Y = BF_4).[13b] Deprotonation of the latter with base (aqueous NaOH) regenerates the neutral η^3-azaallyls.

IR and NMR studies on the azaallyl derivatives described herein confirm the presence of a single isomer in solution, for which the *syn*,*endo* configuration (**G**) can be proposed.[7,8] Three doublets of doublets are observed



G

for the relevant protons of the azaallyl moiety, with the observed pattern of these resonances being highly reminiscent of that of η^3-allyls. As would be expected of the interproton couplings within this unit, $^3J_{ac}$ has the greatest value (6.5−7.5 Hz), $^3J_{cs}$ is of intermediate magnitude (3.5−4.5 Hz), and $^2J_{as}$ has the lowest value (0−1.6 Hz), being in some cases unresolved.

The solution structure deduced by spectroscopic means for these complexes has been confirmed in the solid state

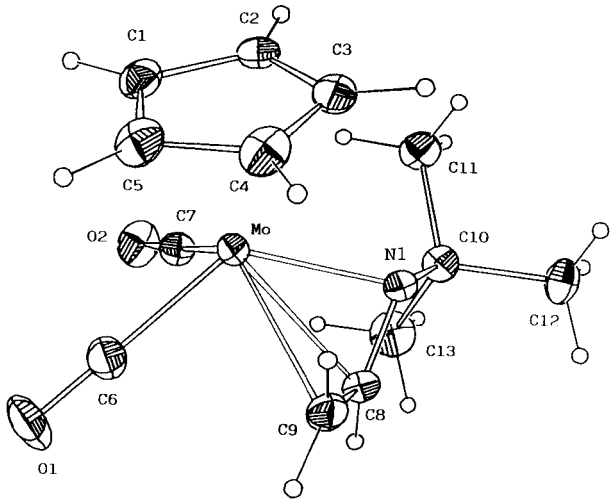


Figure 1. ORTEP view and atom labeling scheme of compound **1az**.

Table 1. Crystal and Refinement Data for 1az and 9cad

formula	$C_{13}H_{17}NO_2Mo$	$C_{13}H_{17}O_3NW$
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	$P2_1/n$
cell dimensions		
a, Å	31.388(3)	8.953(2)
b, Å	7.3980(7)	13.928(3)
c, Å	12.175(2)	11.678(2)
β, deg	106.00(1)	95.74(2)
Z	8	4
V, Å^3	2717.6(6)	1449.0(9)
D_{calcd}, g cm^{-3}	1.54	1.921
F(000)	1280	800
temp, K	295	290
μ(Mo *K*α), cm^{-1}	9.32	8.14
cryst dimens, mm	0.20 × 0.20 × 0.30	0.30 × 0.22 × 0.53
diffractometer	Enraf-Nonius CAD4	Rigaku AFC6S
radiation	graphite-monochromated Mo *K*α (λ = 0.710 69 Å)	graphite-monochromated Mo *K*α (λ = 0.710 69 Å)
scan technique	$\omega/2\theta$	$\omega/2\theta$
data colld	(−37,0,0) to (37,8,14)	(0,0,−12) to (9,14,11)
no. of reflns coll	2814	2156
no. of unique data	2367	2011
no. of obsd reflns	2230($I \geq 2\sigma$I)	1562($I > 3\sigma$I)
R_{int} (%)	1.3	5.4
standard reflns	3/102	3/200
$R = \sum\|\Delta^2F\|/\sum\|F_o\|$	2.0	2.9
$R_w = (\sum w\Delta^2F/\sum w\|F_o\|^2)^{1/2}$	2.8	3.6
average shift/error	0.02	0.02

via an X-ray diffraction study carried out with the compound **1az**. Figure 1 shows an ORTEP diagram of the molecule, crystallographic data and important bond lengths and angles are collected in Tables 1 and 2. The structure can be described as a distorted "four-legged piano-stool", with the η^3-1-azaallyl unit formally occupying two coordination sites. The bond distances within the Mo−η^3-1-azaallyl linkage are Mo1−C8 = 2.317(3); Mo1−C9 = 2.288(4), and Mo1−N1 = 2.227(3) Å. These values compare well with the corresponding distances in other η^3-azaallyl derivatives of Group 6 metals that have been authenticated by X-ray crystallography (*e.g.*, 2.299(6), 2.286(5), and 2.186(5) Å, respectively, in Cp*W(η^3-CH_2CHNEt)$(CO)_2$[7a]). The N-bound *t*-Bu group of the azaallyl adopts a *syn* orientation, possibly to minimize adverse steric interactions with the cyclopentadienyl ring. The N atom N1, forms two N−C bonds, one single at 1.493(4) Å (N1−C10) and the other appreciably shorter (N1−C8 = 1.323(4) Å). The latter distance is intermediate between typical values for single (e.g., 1.44 Å) and double (1.27 Å) C−N bonds, this

Table 2. Selected Bond Distances and Angles for 1az

Bond Distances (Å)			
Mo1−N1	2.227(3)	O1−C6	1.160(5)
Mo1−C6	1.948(4)	O2−C7	1.167(4)
Mo1−C7	1.940(3)	C8−C9	1.385(5)
Mo1−C8	2.317(3)	C10−C11	1.522(5)
Mo1−C9	2.288(4)	C10−C12	1.522(6)
N1−C8	1.323(4)	C10−C13	1.530(5)
N1−C10	1.493(4)		
Bond Angles (deg)			
C8−Mo1−C9	35.0(1)	Mo1−C6−O1	179.4(3)
C7−Mo1−C9	120.2(1)	Mo1−C7−O2	173.7(3)
C7−Mo1−C8	93.0(1)	Mo1−C8−N1	69.4(2)
C6−Mo1−C9	79.5(1)	N1−C8−C9	117.6(3)
C6−Mo1−C8	93.1(1)	Mo1−C8−C9	71.3(2)
C6−Mo1−C7	76.4(1)	Mo1−C9−C8	73.7(2)
N1−Mo1−C9	61.7(1)	N1−C10−C13	114.8(3)
N1−Mo1−C8	33.8(1)	N1−C10−C12	105.4(3)
N1−Mo1−C7	90.5(1)	N1−C10−C11	108.1(3)
N1−Mo1−C6	125.1(1)	C12−C10−C13	109.3(3)
Mo1−N1−C10	131.3(2)	C11−C10−C13	110.8(3)
Mo1−N1−C8	76.9(2)	C11−C10−C12	108.6(3)
C8−N1−C10	120.0(3)		

comparatively short bonding interaction constituting further evidence for electron delocalization along the C9−C8−N1 skeletal frame and, hence, for the η^3-bonding mode of the azaallyl fragment. Also, the value of 120.0(3)° observed for the C8−N1−C10 angle is a clear indication of sp^2-hybridization at nitrogen.

Transformation of Methyl−M−Isocyanide Complexes in Solvents of Different Donor Capacity. The room temperature addition of MeI to a THF solution of the metalate salt Na[Cp*Mo$(CO)_2$(CN-*i*-Pr)] results in the rapid, quantitative formation of the η^2-iminoacyl Cp*Mo(η^2-C(=N-*i*-Pr)Me)$(CO)_2$ (**4im**) as the only detectable product. However, when this reaction was conducted at low temperature (−60 °C) in an NMR tube, both ^{1}H and ^{13}C{^{1}H} NMR spectra showed that the formation of a *kinetic* mixture of *cis*- and *trans*-Cp*MoMe$(CO)_2$(CN-*i*-Pr) (**4al**) had occurred in an approximate ratio of cis:trans = 1:1.8. As the probe temperature was raised to −10 °C, the signals associated with the cis isomer diminished in intensity relative to those of the trans methyl, with simultaneous appearance of signals due to the η^2-iminoacyl product **4im** ($t_{1/2}$ = *ca.* 5 min). A further increment of 10 °C in the temperature resulted in a mixture of only *trans*-**4al** plus **4im**, while at 18 °C, resonances due to the trans alkyl diminished

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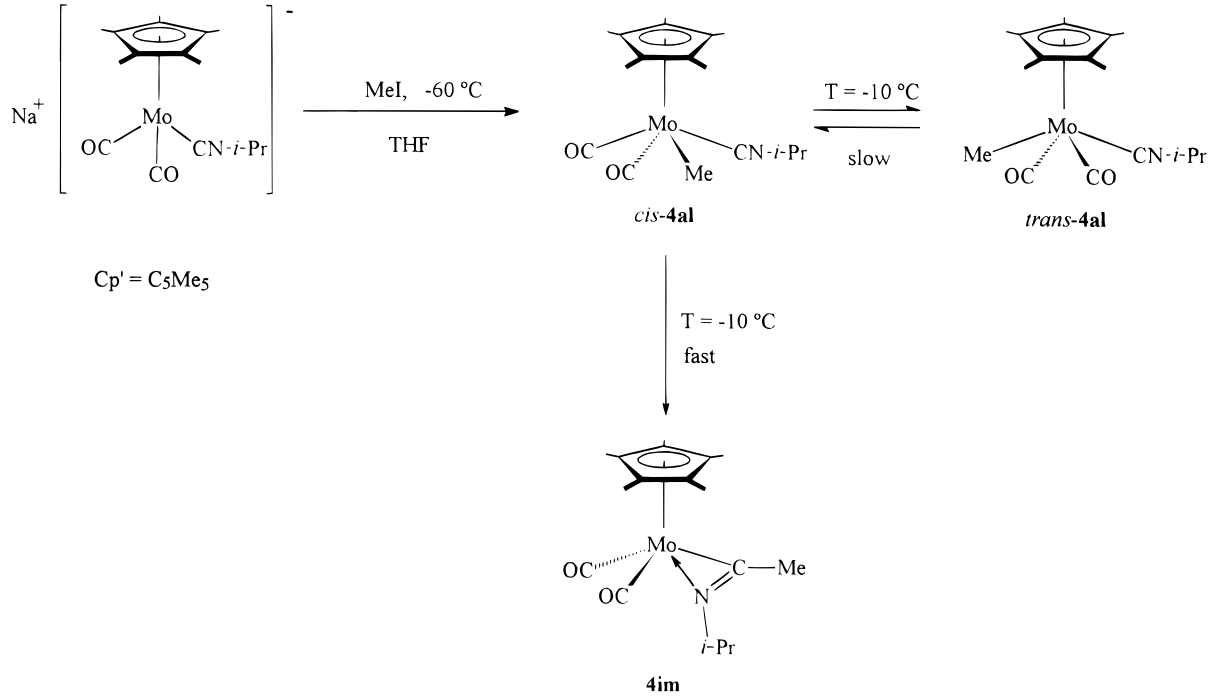
(16) (a) Filippou, A. C.; Völkl, C.; Kiprof, P. *J. Organomet. Chem.* **1991**, *415*, 375. (b) Filippou, A. C.; Völkl, C.; Rogers, R. D. *J. Organomet. Chem.* **1993**, *463*, 135.

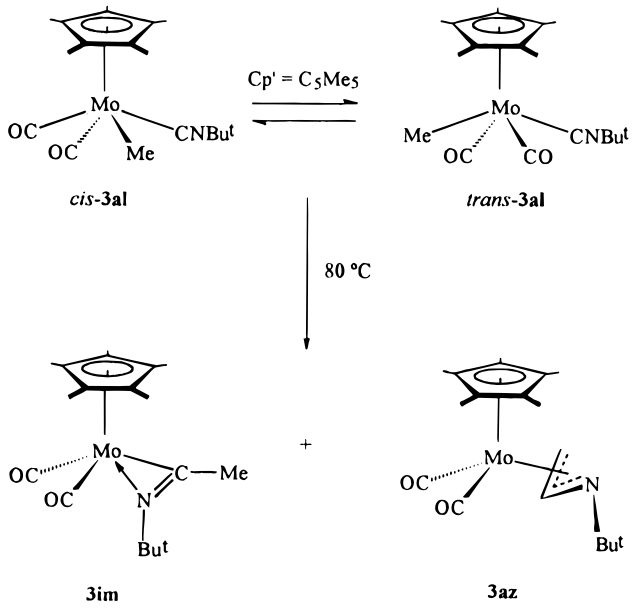
Scheme 2



($t_{1/2}$ = *ca.* 6 min) to afford **4im** as the only detectable product. These findings clearly demonstrate that it is the cis isomer only which undergoes the migratory insertion reaction,[17] cis−trans isomerization being a slower process than the migratory insertion of the cis isomer for this particular metal and ligand combination (Scheme 2). In such a case, it is clear that a thermodynamic distribution of cis and trans methyls cannot be obtained. The observed ratio thus reflects only the kinetic proportion of each which results from electrophilic attack of MeI at the metal center.

Important solvent effects have been noted in both the Mo and the W system. In general, nonpolar solvents increase the amount of the azaallyl formed. For the W complexes, η^2-iminoacyl formation appeared less facile and only in pyridine and methanol, the more polar of the solvents used, was iminoacyl generation significant (30% and >98%, respectively, the reaction in methanol occurring at a noticeably faster rate). The thermolysis of the molybdenum complex **3al** in a range of solvents provides useful information on the role of the solvent in the isomerization reaction (Table 3). Poor donor solvents, such as aromatic hydrocarbons or diethyl ether, provided the η^3-azaallyl **3az** almost exclusively, while the more polar and better coordinating solvents, like THF, acetone, acetonitrile, or pyridine, strongly favored the formation of **3im**. Following Bergman's work,[18b] a series of methyl-substituted tetrahydrofurans and 2,6-dimethylpyridine were also employed as thermolysis solvents. These solvents display a donor ability distinct to the unsubstituted parent solvents, THF and pyridine, respectively, and were found not to encourage

Table 3. Relative Ratio (%) of η^3-Azaallyl (3az) to η^2-Iminoacyl (3im) Formation in the Thermolysis of 3al in a Range of Solvents[a]



solvent	**3az**:**3im**
benzene	>95:<5
diethyl ether	>95:<5
thf	20:80
2-MeTHF	80:20
2,5-Me_2THF	90:10
2,2,5,5-Me_4THF	>95:<5
acetone	<5:>95
acetonitrile	<5:>95
pyridine	<5:>95
2,6-dimethylpyridine	>95:<5

[a] Samples of **3al** were thermally transformed (80 °C), and the respective ratios of products were obtained by ^{1}H NMR spectroscopy (C_6D_6) (see Experimental Section).

generation of **3im** and, hence, to preferentially develop the azaallyl **3az**. Clearly then, solvents with an efficient Lewis base capacity induce η^2-iminoacyl formation.[18] A

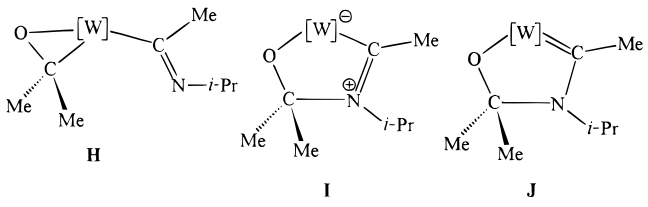
(17) (a) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (c) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410.

(18) (a) Butler, I. S.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1967**, *6*, 2074. (b) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028. (c) Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345. (d) Cotton, J. D.; Latif, L. *Inorg. Chim. Acta* **1981**, *47*, 171. (e) Cotton, J. D.; Kroes, M. M.; Markwell, R. D.; Miles, E. A. *J. Organomet. Chem.* **1990**, *388*, 133. (f) Bent, T. L.; Cotton, J. D. *Organometallics* **1991**, *10*, 3156.

detailed kinetic study of these reactions in different solvents and solvent mixtures has been accomplished, the results of which, including a thorough mechanistic discussion, will be published in a future report.[19] Here, we conclude that the tendency of methyl−M−isocyanides of the general type Cp′MMe(CO)$_2$(CNR) to transform into the η^2-iminoacyl products Cp′M(η^2-C(=NR)-Me)(CO)$_2$ at the expense of the alternative η^3-azaallyl derivatives Cp′M(η^3-CH$_2$C(H)NR)(CO)$_2$ is greater for (i) Mo vs W, (ii) the less bulky isocyanides, and (iii) the stronger donor solvents. A less pronounced preference for the Cp* derivatives, as compared to the Cp analogues, have been observed in some of the cases studied.

Formation of Cycloaddition Products by Thermolysis of Methyl−M−Isocyanides of Tungsten in Acetone. In contrast with the thermal behavior of the complexes Cp′WMe(CO)$_2$(CN-*t*-Bu) (**5al** and **6al**), in acetone, which gave complicated mixtures of unidentified products, thermolysis (90 °C) in that solvent of the CN-*i*-Pr derivative **8al** generated the expected mixture of **8im** and **8az** (*ca.* 3.2:1 ratio). However, when this reaction was monitored by ^{1}H NMR spectroscopy (acetone-d_6), a series of signals corresponding to a fourth species (denoted **8cad**) was observed to grow into the spectrum, its characteristic resonances reaching a maximum intensity of *ca.* 11% of the total intensity after heating for 4 min at 90 °C. The concentration of this hitherto unobserved species subsequently diminished, but no other additional compounds were formed, which may be taken to indicate that under these conditions, **8cad** converted into one (or both) of the anticipated products, **8im** and **8az**. At somewhat lower temperatures (50 °C), the rate of formation of **8cad** was seen to be superior to those of **8im** and **8az** and, in addition, comparatively little decrease in its concentration was observed, even over an extended period at that temperature. Pure compound **8cad** was obtained following low temperature (−30 °C) column chromatography, using neutral alumina as the static phase. NMR experiments vide infra showed the presence of the Cp*, CN-*i*-Pr, CO, and Me functionalities and confirmed, in addition, that the W−Me group had migrated onto the isocyanide carbon to give an iminoacyl fragment. Moreover, they clearly indicated the incorporation of a molecule of acetone with the C−O carbon nucleus resonating at δ 109.3.

Two possible formulations may be envisaged for this product, namely an η^2-acetone adduct[20] of a monohapto W−iminoacyl **H** or a metallacyclic structure **I** derived from a [3 + 2] cycloaddition of the W−C(=N-*i*-Pr)Me fragment to a molecule of acetone. Precedent for the



latter possibility can be found in previous work by Werner and co-workers.[9,21] In order to unambiguously characterize this material, X-ray studies were attempted. While crystals of **8cad** suitable for this determination could not be obtained, the related complex **9cad**, isolated after the analogous reaction of CpWMe(CO)$_2$(CNMe) (**9al**) in acetone, readily provided single crystals. Figure 2 shows the molecular structure of the compound, Tables 1 and 4 contain, respectively, crystallographic data and pertinent bond distances and angles. As may be seen, this diffraction study reveals

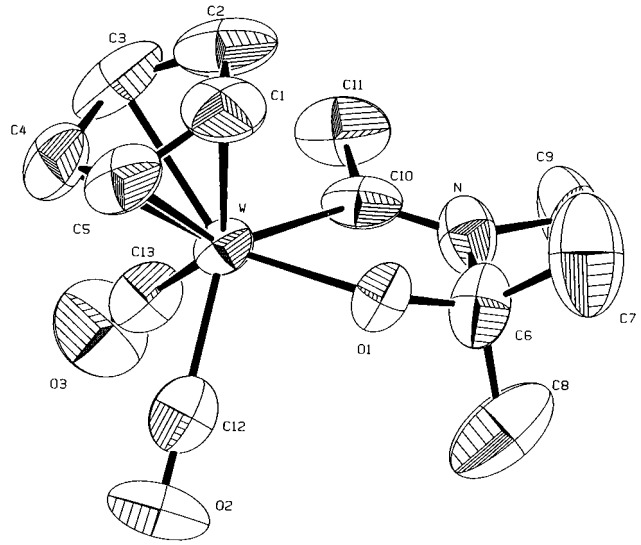


Figure 2. ORTEP view and atom labeling scheme of compound **9cad**.

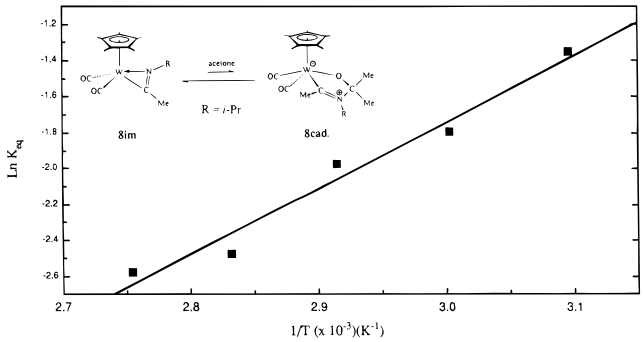


Figure 3. Plot of ln(K) vs 1/*T* for the equilibrium between **8im** and **8cad**.

Table 4. Selected Bond Distances and Angles for 9cad

Bond Distances (Å)			
W−O1	2.074(6)	N−C6	1.54 (1)
W−C10	2.124(9)	N−C9	1.46 (1)
W−C12	2.00 (1)	N−C10	1.29 (1)
W−C13	1.94 (1)	C6−C7	1.54 (2)
O1−C6	1.32 (1)	C6−C8	1.52 (2)
O2−C12	1.13 (1)	C10−C11	1.54 (1)
O3−C13	1.16 (1)		
Bond Angles (deg)			
O1−W−C10	73.0(3)	O1−C6−C7	110.3(9)
O1−W−C12	82.5(3)	O1−C6−C8	112.0(1)
O1−W−C13	131.4(3)	N−C6−C7	108.0(1)
C10−W−C12	118.0(4)	N−C6−C8	106.1(9)
C10−W−C13	82.0(4)	C7−C6−C8	113.0(1)
C12−W−C13	73.4(4)	W−C10−N	119.2(6)
W−O1−C6	122.2(6)	W−C10−C11	124.1(7)
C6−N−C9	119.0(1)	N−C10−C11	116.7(9)
C6−N−C10	114.5(7)	W−C12−O2	177.3(9)
C9−N−C10	127.0(1)	W−C13−O3	179.0(1)
O1−C6−N	107.9(8)		

(19) Daff, P. J.; Poveda, M. L.; Carmona, E. Manuscript in preparation.

(20) (a) Huang, Y.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298. (b) Delbecq, F.; Sautet, P. *J. Am. Chem. Soc.* **1992**, *114*, 2446 and references cited therein.

(21) For others transformations of acetone in transition metal chemistry, see: Kukushkin, V. Y.; Belsky, V. K.; Tudela, D. *Inorg. Chem.* **1996**, *35*, 510.

that **9cad** (and by inference **8cad**) exists in the solid state as a heterometallacycle $CpW(\eta^2(C,O)$-$C(Me)=N(Me)C(Me)_2O)(CO)_2$, formally the product of the 1,3-dipolar addition[22] of the W−C(=NMe)Me moiety to a molecule of acetone, probably after η^1(O)-coordination.

The Cp ligand in **9cad** is coordinated in the usual η^5-fashion, resulting in an approximate four-legged pianostool geometry about the W center. Possibly due to the steric demands of the five-membered heterometallacycle, the angle subtended at the W atom by the two carbonyl ligands is rather acute, being only 73.4(4)°. Despite the nonsymmetric nature of the ring (C and O donor atoms), the two W−CO bond lengths are almost identical within experimental error (1.94(1) and 2.00(1) Å). The W−C(10) bond length (2.124(9) Å) is shorter than that expected for a typical alkylic carbon−tungsten(II) bond (2.28(1) Å in $W(CH_3)(S_2CNMe_2)(CO)_2(PMe_3)_2$[23a]), longer than that found in high-oxidation state alkylidene complexes (1.88−2.00 Å[23b]), and compares well with some Fischer-type W−carbene compounds (*e.g.*, 2.09(2) Å in $[Tp^*(CO)(PhC{=}CMe)W{=}C(OMe)Bu^n][CF_3SO_3]$).[23c] However, the C−N bond of the iminoacyl fragment within the cyclic unit has a length of 1.29(1) Å, which is clearly in accord with the existence of a C=N double bond (1.26−1.31 Å in organic molecules).[23d] Thus, we conclude that such cycloadducts are best represented by the zwitterionic structure **I**, with only a small contribution of the alternative carbenic form **J**.

By far the most interesting feature of the structure is the metallaheterocyclic ligand functionality. As already pointed out, this type of unit has been encountered in some Cp−Co complexes[9] and authenticated by X-ray methods in the compound $[CpCo(\eta^2(C,O)$-$C(Me)=N(Me)C(Me)_2O)(PMe_3)]I$, the preparation of which bears strong similiarities to that of the compounds described herein. In the cobalt complex, the Co−C−N−C part of the cycle was found to be almost planar, the O atom lying 0.34 Å out of this plane directed toward the PMe_3 ligand. Compound **9cad** shows an analogous distortion from planarity within the cycle. The plane containing atoms W, O1, and C6 form an angle of 19.7° with that defined by W, C10, N, and C6, the oxygen atom tending toward the Cp ring and lying 0.26 Å out of the former plane. The angle C10−W−O1 in **9cad** is 73.0(3)°, while the analogous angle in the cobalt compound has a value of 82.3(4)°. Clearly, compound **9cad** possesses a more closed structure, no doubt reflecting its more constrained environment due to the presence of two ancillary ligands as opposed to one in $[CpCo(\eta^2(C,O)$-$C(Me)N(Me)C(Me)_2O)(PMe_3)]I$.[9]

Thermolysis of **8cad** in C_6H_6 (70 °C) released 1 equiv of acetone from the complex in a clean transformation ($t_{1/2}$ = *ca.* 20 min) that gave **8im** as the only product; no η^3-azaallyl **8az** was produced during this reaction. In acetone solvent, however, thermolysis resulted in the attainment of an equilibrium between **8cad** and **8im** which strongly favors **8im**. The equilibrium constant K_{eq} was measured over a ΔT = 40 °C range (Figure 3), allowing the determination of the free enthalpy and entropy of reaction, $\Delta H° = 30$ kJ/mol and $\Delta S° = -106$ J/(mol·K). As would be expected, at higher temperatures, the position of the equilibrium drifts to the left. At lower temperatures (room temperature and below), the extrusion of acetone does not occur at an appreciable rate and this allows the study of the characteristic fluxionality of the complex.

At −30 °C, the methyl protons of the included molecule of acetone appear as two singlets at δ 1.06 and 1.29 ($C_6D_5CD_3$ solvent), in accord with the proposed structure. However, these signals coalesce at higher temperatures to give a broad resonance at 20 °C (δ 1.17). Similarly, the methyl groups of the *i*-Pr residue are also diastereotopic at −30 °C, but result in only one signal at ambient temperature. Although no quantitative data are available, these two exchange processes would appear to be interconnected. In view of the aforementioned observations regarding the liberation of acetone from the coordination sphere of compound **8cad**, a possible explanation for the observed fluxionality invokes a comparatively labile acetone−iminoacyl C−N linkage. The fluxional behavior could then involve the temporary fission of this acetone−iminoacyl C−N bond, followed by rapid cis to trans equilibration of the resulting η^1-iminoacyl σ-acetone adduct (mechanism **a**, Scheme 3). An alternative, and simpler, explanation invokes a robust C−N bond, with the fluxionality being explained in a simplified manner by a pseudorotation of the intact metallaheterocyclic unit about an axis passing through the metal and the midpoint of the C−N single bond (pathway **b**). This latter process finds support in the well-known mechanism of cis−trans isomerization in Cp′ containing square pyramidal structures.[24] It should be emphasized that for pathway **a** to be a valid explanation of the observed fluxionality, then the cis−trans isomerization of the intermediate must be rapid in comparison with its collapse to the cycloadduct. Otherwise, the exchange rates of the two pairs of methyls would be expected to be different. For either of these redistributions, an effective mirror plane of symmetry would be created in the transient species, thus explaining the magnetic equivalence (at higher temperatures) of the originally diastereotopic methyls of the $-OCMe_2-$ and $-CHMe_2$ groups.

To distinguish between the two interpretations, the spectroscopic behavior of the related derivative $Cp^*W(\eta^2(C,O)$-$C(Me)N(Et)CH(Me)O)(CO)_2$ (**10cad**), which incorporates a molecule of acetaldehyde, was investigated (Scheme 4). The preparation of **10cad** was accomplished by a method entirely analogous to that of the other W metallaheterocycles. Its ^{1}H NMR spectrum recorded in $C_6D_5CD_3$ at −40 °C reveals the presence of the two expected diastereomers in an approximate 4:1 molar ratio (aldehyde proton at δ 5.54 and 4.98, respectively). At the above temperature, the diastereotopic methylene protons of the ethyl substituent appear as two multiplets at δ 2.66 and 2.36 with the same 4:1 intensity ratio (J_{gem} = 14 Hz). This is consistent with the existence of two distinct species, each possessing an inequivalent CH_2 pair.

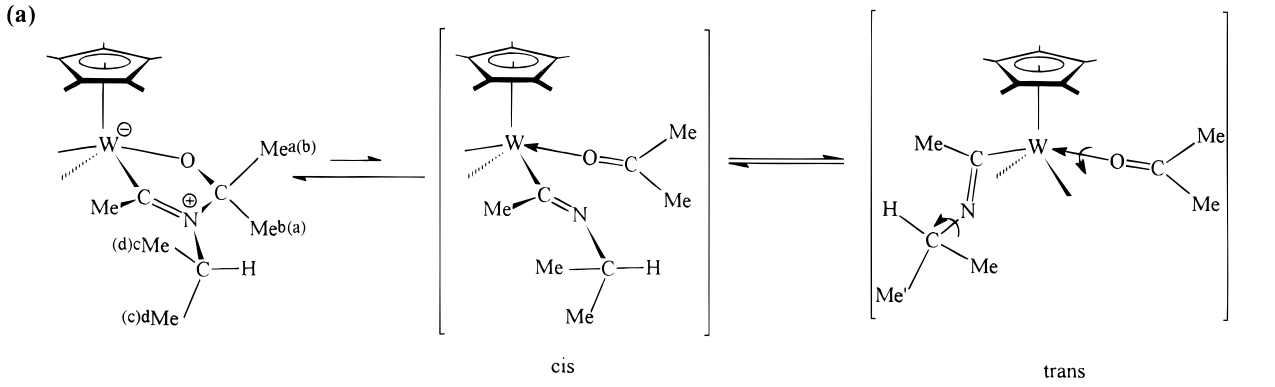
The two diastereomers interchange rapidly at higher temperatures (Scheme 4), and in the fast exchange

(22) Alvarado, Y.; Daff, P. J.; Perez, P. J.; Poveda, M. L.; Sánchez-Delgado, R.; Carmona, E. *Organometallics* **1996**, *15*, 2192 and references therein.

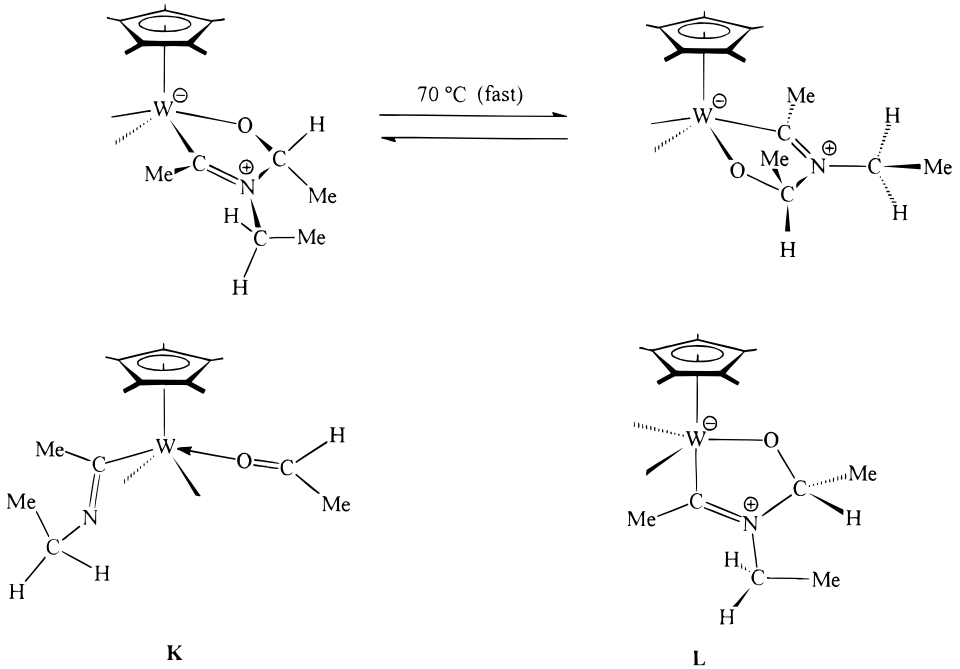
(23) (a) Carmona, E.; Contreras, L.; Poveda, M. L.; Sánchez, L. J.; Atwood, J. L.; Rogers, R. D. *Organometallics* **1991**, *10*, 61. (b) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986; Vol. 1, Chapter 3. (c) Feng, S. G.; White, P. S.; Templeton, J. L. *Organometallics* **1993**, *12*, 2131. (d) Sandorfy, C. In *The Chemistry of the Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Wiley: New York, 1970; Chapter 1.

(24) Adams, R. D.; Cotton, F. A. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 12.

Scheme 3



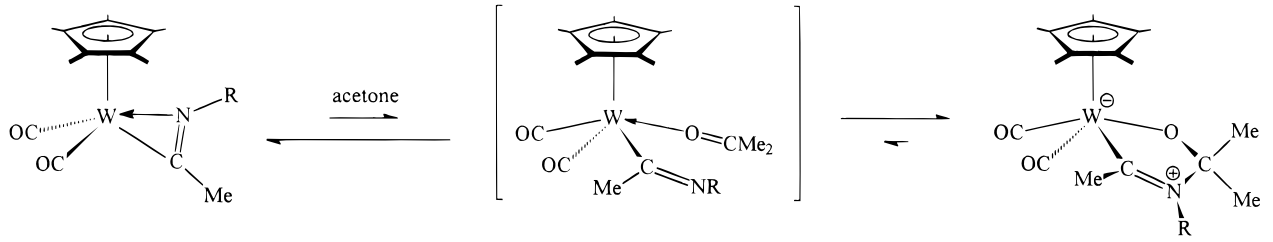
Scheme 4



regime (70 °C), a single quartet at δ 5.30 is observed for the aldehyde proton, MeC*H*O, with a corresponding sharp doublet at δ 0.97 assigned to the accompanying methyl group. Under these conditions, the NCH_2Me signal is a multiplet centered at δ 2.76; subsequent decoupling of the adjacent Me group (triplet at δ 0.63) converts the CH_2 multiplet into an AB spin system (δ_A = 2.68, δ_B = 2.78 ppm; $^2J_{AB}$ = 14 Hz). Clearly then, since even under the conditions of rapid isomer exchange, these protons remain inequivalent; the interconversion mechanism of these cycloaddition products must involve a rotation of the intact heterocyclic unit about an axis passing through W and the center of the C−N single bond and not the cleavage of this bond (*i.e.*, structure **L** must be the key intermediate in the observed process and *not* **K**, which would be anticipated to possess an effective plane of symmetry and, thus, interconvert the two diastereomeric pairs). It also has to be noticed that according to this proposed mechanism, enantiomeric structures are not interconverted; this has been specified in Scheme 4. However, cleavage of the C−N bond does indeed occur at higher temperatures on the laboratory time scale; this aspect will be discussed subsequently.

In an attempt to ascertain whether the cycloaddition products could be prepared from the η^2-iminoacyls, the

Scheme 5



compounds Cp′W(η^2-C(=NR)Me)$(CO)_2$ (R = Me, Et, *i*-Pr, *t*-Bu) were reacted with acetone at *ca.* 50 °C. Under conditions at which the N−methyl and N−ethyl complexes gave the corresponding cycloadducts quantitatively, the sterically more hindered N−*iso*propyl compounds provided equilibrium mixtures of **cad** and **im** derivatives and the N−*tert*-butyl compounds did not afford cycloadducts at all. The origin of this effect is not immediately apparent but may be traced to steric effects within the five-membered ring of the cycloadducts, which for the *tert*-butyl derivatives, destabilize such cycles with respect to the sterically less hindered η^2-iminoacyls. With respect to the cycloaddition process, it would appear probable that it occurs via an η^1-acetone, η^1-iminoacyl intermediate species (Scheme 5), subsequent coupling of the adjacent acetone and iminoacyl fragments leading directly to the cycloaddition products. An interesting point which indicates important differences between these complexes and those described by Werner[9] is the lack of exchange between incorporated acetone and solvent acetone. Indeed, significant acetone-h_6/acetone-d_6 scrambling was only apparent after heating **8cad** at 60 °C for 3−4 h. We conclude that this exchange is not occurring significantly in a bimolecular process at the η^1-acetone intermediate stage, but rather is dependent upon the nucleophilic attack of acetone upon the η^2-iminoacyl **8im**. Thus, scrambling of acetone only becomes significant as the system approaches equilibrium and not before.

In summary, we have shown that the reaction of the Mo and W metalates $[Cp'M(CO)_2(CNR)]^-$ with MeI can yield a variety of products in addition to the Me−M−CNR derivatives that result from the initial attack of the electrophile on the metal. Subsequent intramolecular redistributions of these methyl complexes give rise to η^2-iminoacyls (structure **C**), η^3-1-azaallyls (**E**), or [3 + 2] cycloaddition (to acetone) products (**F**). Importantly, in none of the thermal transformations studied was η^2-acyl formation observed, such fragments would be the result of methyl migration to a carbonyl ligand.[1] While kinetic factors may play an important role in predetermining which of the two types of unsaturated ligand present in these complexes actually experiences the migratory insertion reaction, recent results from this laboratory strongly support the assertion that carbonyl−η^2-iminoacyl structures are thermodynamically favored over their isomeric isocyanide−η^2-acyl counterparts.[25] In addition, it is worth pointing out that while the reactivity reported herein focusses upon systems which may be regarded as being "classical" in the sense that they have been extensively studied over a period of at least 20 years,[10,11] the Mo and W η^3-1-azaallyls have escaped observation until comparatively recently.[7,8] Equally notable is the fact that the heterometallacycles reported herein have eluded detection[7,10,11] until the realization of this study.

Experimental Section

Microanalyses were by Pascher, Microanalytical Laboratory, Remagen, Germany, and by the Analytical Services of the University of Sevilla. Infrared spectra were obtained from Perkin Elmer spectrometers, models 577 and 684. The NMR instruments were Bruker AMX-500, Bruker AMX-300 and Varian XL-200 spectrometers. Spectra are referenced to external $SiMe_4$ ($\delta = 0$ ppm) using the residual protio solvent peaks as internal standards (^{1}H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropriate. All manipulations were performed under dry, oxygen-free dinitrogen either in a Vacuum Atmospheres drybox or by following conventional Schlenk techniques.[26] All solvents were appropriately dried and degassed immediately prior to use. Silica gel for column chromatography was Merck 230−400 mesh. The alumina used for low-temperature columns was neutral, active Merck 70−230 mesh and was oven-dried for 24 h and degassed overnight under dynamic vacuum prior to use. The cryostat employed in the low-temperature chromatography experiments was a Haake model KT90 which circulated ethanol through jacketed glassware. The compounds pentamethylcyclopentadiene,[27] $Cp'M(CO)_3I$,[28] CNMe,[29] CNEt,[29] and CN-*t*-Bu[30] were prepared according to literature methods and checked for purity before use. The compound $Cp^*WMe(CO)_2(CNEt)$ was prepared by the method described below; it was characterized by comparison of its NMR spectra with those reported by Filippou et al.[7a] Other reagents were purchased from commercial suppliers and were used as received. The iodide dicarbonyl−isocyanide compounds $Cp'M(CO)_2(CNR)I$ (Cp′ = η^5-C_5H_5, η^5-C_5H_4Me, η^5-C_5Me_5; M = Mo, W; CNR = alkylisocyanide) were obtained by a modified version of a published procedure,[31] the details of which are as follows.

In a typical preparation, 10 mmol of red $Cp'M(CO)_3I$ powder together with a catalytic amount (*ca.* 20 mg) of the red tricarbonyl dimer $[CpMo(CO)_3]_2$ were dissolved in 100 mL of benzene. To the resulting dark red solution at room temperature was added 1 equiv of isocyanide via syringe. The mixture was then heated to 80 °C in an oil bath with vigorous stirring. Typically, the reaction began at an oil bath temperature of 60 °C and was evidenced by the evolution of CO gas.

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The time to completion varied, depending upon the system and the amount of $[CpMo(CO)_3]_2$ catalyst added initially, but generally was within a period of 1 h. The progress of the reaction could be monitored by solution IR spectroscopy, the sharp CO absorption at *ca.* 2050 cm^{-1} assigned to $Cp'M(CO)_3I$ reducing to zero intensity as a new, broader, strong absorption assigned to the terminal isocyanide stretching vibration grew into the spectrum at *ca.* 2150 cm^{-1}.

After completion of the reaction, solvent and volatiles were removed *in vacuo* and the resulting oily dark red residue was redissolved in 40 mL of THF. Purification was achieved by passage through a column (40 × 5 cm) packed with silica gel. Elution with diethyl ether recovered the product as a dark red solution, which was evaporated to dryness to give a red powder. The product may be crystallized from diethyl ether, but the crude red powder was found to be sufficiently pure (95% by NMR) for our purposes. This general methodology proved to be universally applicable to the preparation of all compounds of the generic class $Cp'M(CO)_2(CNR)I$ (M = Mo, W). The spectroscopic data of the products were fully in accord with published work.[7,8c,10a,11,27,30] In these laboratories, gram quantities of $Cp'M(CO)_2(CNR)I$ (up to 10 g) were routinely prepared in under 3 h.

Preparation of the *σ*-Methyl−Isocyanide Complexes $CpMoMe(CO)_2$(CN-*t*-Bu) (1al), $(MeCp)MoMe(CO)_2$(CN-*t*-Bu) (2al), $Cp^*MoMe(CO)_2$(CN−*t*-Bu) (3al), $CpWMe(CO)_2$(CN-*t*-Bu) (5al), $Cp^*WMe(CO)_2$(CN-*t*-Bu) (6al), $CpWMe(CO)_2$(CN−*i*-Pr) (7al), $Cp^*WMe(CO)_2$(CN-*i*-Pr) (8al), $CpWMe(CO)_2$(CNMe) (9al), and $Cp^*WMe(CO)_2$(CNEt) (10al). Essentially the same experimental procedure was employed in the preparations of these compounds; the representative synthesis of $Cp^*MoMe(CO)_2$(CN-*t*-Bu) (**3al**) was as follows.

The complex $Cp^*Mo(CO)_2$(CN-*t*-Bu)I (3.0 g, 6.0 mmol) was dissolved in 50 mL of THF, the resulting red solution was transferred onto a 1% Na/Hg amalgam containing 0.3 g (13 mmol) of Na at room temperature, and the mixture stirred for a period of 2 h. During that time, the solution became a pale yellow color and a finely divided white precipitate of NaI could be observed. The solution was decanted from the mercury into a clean vessel and cooled to −78 °C. Methyl iodide (0.6 mL, 6.5 mmol) was added with stirring, no color change was observed, although the reaction in all cases studied spectroscopically was found to be complete within the time of mixing at that temperature (*vide infra*). After the reaction mixture was stirred for 5 min the bath temperature was raised to 0 °C and the solvent was removed completely *in vacuo* (*ca.* 2 h), giving a yellow/brown oily solid. The product was redissolved in Et_2O (40 mL) and separated from the inorganic byproducts by filtration, addition of petroleum ether, followed by a reduction in volume to 20 mL, generating a supersaturated solution, which upon cooling to −30 °C overnight furnished yellow/orange crystals of **3al**, which were rinsed with cold petroleum ether and dried *in vacuo*. As was found to be the case for some of the compounds of this class, **3al** slowly transforms in the solid state to give quantitatively the η^2-iminoacyl **3im** at ambient temperature over a period of 2−3 weeks; thus, pure **3al** was stored under an inert atmosphere at −30 °C, at which temperature this transformation occurred with a negligible rate. Yield 1.8 g (77%).

$Cp^*MoMe(CO)_2$(CN-*t*-Bu) (3al). Anal. Calcd for $C_{18}H_{27}NO_2Mo$: C, 56.10; H, 7.01; N, 3.64. Found: C, 56.00; H, 7.16; N, 3.53. IR (Nujol mull, cm^{-1}): 2112 (m), 2060 (sh, ν_{CN}), 1935 (s), 1920 (s), 1822 (s), 1803 (s, ν_{CO}). ^1H NMR (200 MHz, 20 °C, C_6D_6): δ 0.25, 0.47 (s, Mo−Me), 0.90, 1.02 (s, CMe_3), 1.72, 1.73 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR (50 MHz, 20 °C, C_6D_6): δ −12.1, −11.3 (Mo−Me), 9.6, 9.7 (C_5Me_5), 30.0, 30.1 (CMe_3), 87.8 (CMe_3), 100.8, 101.6 (C_5Me_5), 234.4 (2 CO), 240.0, 253.5 (CO), isocyanide Mo−C signals not observed.

$CpMoMe(CO)_2$(CN-*t*-Bu) (1al). Yellow crystals. Yield 60%. Anal. Calcd for $C_{13}H_{17}NO_2Mo$: C, 49.52; H, 5.40; N, 4.44. Found: C, 49.65; H, 5.59; N, 4.35. IR (Nujol mull, cm^{-1}): 2110 (m, ν_{CN}), 1954 (s), 1899 (s, ν_{CO}). ^1H NMR (300 MHz, 20 °C, C_6D_6): δ 0.49, 0.63 (s, Mo−Me), 0.91, 0.94 (s, CMe_3), 4.68, 4.78 (s, C_5H_5). $^{13}C\{^1H\}$ NMR (50 MHz, 20 °C, C_6D_6): δ −22.3, −20.9 (Mo−Me), 29.7, 29.8 (CMe_3), 90.2, 91.0 (C_5H_5), 231.0 (2 CO), 237.5, 251.1 (CO), isocyanide CMe_3 and Mo−C signals not observed.

$(MeCp)MoMe(CO)_2$(CN-*t*-Bu) (2al). Yellow crystals. Yield 68%. Anal. Calcd for $C_{14}H_{19}NO_2Mo$: C, 51.06; H, 5.78; N, 4.26. Found: C, 50.66; H, 5.67; N, 4.07. IR (Nujol mull, cm^{-1}): 2120 (m), 2060 (sh, ν_{CN}), 1932 (br, s), 1877 (br, s, ν_{CO}). ^1H NMR (500 MHz, 20 °C, C_6D_6): δ 0.37, 0.52 (s, Mo−Me), 0.95, 1.00 (s, CMe_3), 1.65, 1.66 (s, CH_3), 4.60, 4.66, 4.70, 4.75 (overlapping multiplets, C_5H_4Me). $^{13}C\{^1H\}$ NMR (50 MHz, 20 °C, C_6D_6): δ −19.2, −17.3 (Mo−Me), 12.4, 12.6 (*Me*−Cp), 29.7, 29.8 (CMe_3), 57.5 (CMe_3), 87.1, 87.2, 88.6, 88.7, 90.8, 91.8, 93.1 (C_5H_4Me), 167.4 (Mo−CN), 232.1 (2 CO), 238.0, 251.5 (CO).

$CpWMe(CO)_2$(CN-*t*-Bu) (5al). Yellow crystals. Yield 82%. Anal. Calcd for $C_{13}H_{17}NO_2W$: C, 38.71; H, 4.22; N, 3.47. Found: C, 39.05; H, 4.26; N, 3.14. IR (KBr pellet, cm^{-1}): 2110 (s), 2060 (sh, ν_{CN}), 1950 (s), 1860 (br, s, ν_{CO}). ^1H NMR (300 MHz, 20 °C, C_6D_6): δ 0.55, 0.70 (s, W−Me), 0.95, 0.99 (s, CMe_3), 4.65, 4.76 (s, C_5H_5). $^{13}C\{^1H\}$ NMR (50 MHz, 20 °C, C_6D_6): δ −34.6, −34.1 (W−Me), 30.0 (CMe_3), 88.7, 89.6 (C_5H_5), 221.2 (2 CO), 228.3, 241.5 (CO), isocyanide W−C and CMe_3 signals not observed.

$Cp^*WMe(CO)_2$(CN-*t*-Bu) (6al). Yellow/orange crystals. Yield 73%. Anal. Calcd for $C_{18}H_{27}NO_2W$: C, 45.67; H, 5.71; N, 2.96. Found: C, 44.39; H, 5.86; N, 3.01. IR (Nujol mull cm^{-1}): 2108 (m), 2060 (sh, ν_{CN}), 1925 (sh), 1911 (s), 1865 (s), 1842 (s, ν_{CO}). ^1H NMR (200 MHz, 20 °C, C_6D_6): δ 0.32, 0.55 (s, W−Me), 0.92, 1.06 (s, CMe_3), 1.72, 1.77 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR (50 MHz, 20 °C, C_6D_6): −24.2, −23.9 (W−Me), 9.5, 9.7 (C_5Me_5), 30.4, 30.5 (CMe_3), 57.8 (CMe_3), 99.7, 100.4 (C_5Me_5), 190.3 (2 W−CN), 225.4 (2 CO), 232.4, 244.5 (CO).

$CpWMe(CO)_2$(CN-*i*-Pr) (7al). Brown viscous oil (crystalline at low temperature). Yield 44%. Anal. Calcd for $C_{12}H_{15}NO_2W$: C, 37.02; H, 3.90; N, 3.60. Found: C, 37.20; H, 3.88; N, 3.56. IR (Nujol mull cm^{-1}): 2120 (m, ν_{CN}), 1942 (s), 1882 (s, ν_{CO}). ^1H NMR (200 MHz, 20 °C, C_6D_6): δ 0.63, 0.78 (s, W−Me), 0.92, 0.96 (d, 2 $CHMe_2$, ^3J = 6.5 Hz), 0.97 (d, $CHMe_2$, ^3J = 6.5 Hz), 3.48, 3.57 (septets, $CHMe_2$), 4.79, 4.91 (s, C_5H_5). $^{13}C\{^1H\}$ NMR (50 MHz, 20 °C, C_6D_6): δ −34.6, −34.0 (W−Me), 19.9, 20.0 (3 $CHMe_2$), 45.0, 46.3 (2 $CHMe_2$), 85.5, 86.5 (C_5H_5), 218.4 (2 CO), 225.1, 238.4 (CO), isocyanide W−C signals not observed.

$Cp^*WMe(CO)_2$(CN-*i*-Pr) (8al). Yellow crystals. Yield 83%. Anal. Calcd for $C_{17}H_{25}NO_2W$: C, 44.44; H, 5.45; N, 3.05. Found: C, 43.54; H, 5.51; N, 3.09. IR (Nujol mull, cm^{-1}): 2125 (m, ν_{CN}), 1930 (s), 1910 (s), 1853 (s), 1837 (s, ν_{CO}). ^1H NMR (200 MHz, 20 °C, C_6D_6): δ 0.32, 0.55 (s, W−Me), 0.74, 0.75 (d, $CHMe_2$, ^3J = 6.6 Hz), 0.88 (d, $CHMe_2$, ^3J = 6.5 Hz), 1.72, 1.77 (s, 2 C_5Me_5), 4.34 (septet, $CHMe_2$), 4.19 (septet, $CHMe_2$, ^3J = 6.3 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, 20 °C, C_6D_6): −24.3, −23.7 (W−Me), 9.5, 9.7 (C_5Me_5), 23.6 ($CHMe_2$), 48.0, 49.6 (2 $CHMe_2$), 99.5, 100.4 (C_5Me_5), 225.6 (2 CO), 232.2, 244.6 (CO), isocyanide W−C signals not observed.

$CpWMe(CO)_2$(CNMe) (9al). Orange/brown crystals. Yield 26%. This compound displays significant instability at room temperature. Anal. Calcd for $C_{10}H_{11}NO_2W$: C, 33.24; H, 3.05; N, 3.88. Found: C, 32.83; H, 3.24; N, 3.83. IR (KBr pellet, cm^{-1}): 2147 (m, ν_{CN}), 1904 (s), 1780 (s, ν_{CO}). ^1H NMR (500 MHz, 20 °C, C_6D_6): δ 0.51, 0.68 (s, W−Me), 2.43, 2.48 (s, CNMe), 4.66, 4.79 (s, C_5H_5). $^{13}C\{^1H\}$ NMR (125 MHz, 20 °C, C_6D_6): δ −34.2, −34.1 (W−Me), 29.0, 29.7 (CN*Me*), 89.0, 90.1 (C_5H_5), 158.5, 163.9 (W−CN), 222.6 (2 CO), 228.9, 242.4 (CO).

Characterization of $Cp^*MoMe(CO)_2$(CN-*i*-Pr) (4al) at Low Temperature by Spectroscopic Methods: Preparation of $Cp^*Mo(\eta^2$-C(=N-*i*-Pr)Me)$(CO)_2$ (4im). $Cp^*Mo(CO)_2$(CN-*i*-Pr)I (0.2 g, 0.41 mmol) was dissolved in 30 mL of THF, the resulting red solution was transferred onto a 1% Na/Hg amalgam containing 0.02 g (0.87 mmol) of Na, and the mixture was stirred at room temperature for 2 h. During that time, the solution became yellow in color and a fine precipitate of NaI could be observed. A 5 mL aliquot was removed into a

Schlenk tube and reduced to dryness before being redissolved in THF-d_8 (0.5 mL) and transferred into a 5mm NMR tube; the tube was then immersed in liquid-N_2. The remaining 25 mL of the yellow THF $[Cp^*Mo(CO)_2(CN\text{-}i\text{-}Pr)]^-Na^+$ solution was decanted away from the mercury into a clean vessel, in which it was reduced in volume to *ca.* 2 mL. This solution was then transferred into a 10 mm NMR tube for $^{13}C\{^1H\}$ NMR investigations, already containing a sealed capillary of CD_3OD, the tube was then closed, and the assembly immersed in liquid-N_2. Alkylation of the metalate was achieved in both cases by removing a tube from the Dewar vessel and adding an excess of MeI *via* syringe (*ca.* 0.1 mL), which solidified above the frozen metalate solution. The tube was then gently thawed by finger heat until the matrix had begun to melt; it was then shaken before being introduced into the spectrometer probe, which had been precooled to −60 °C. Routine NMR experiments allowed the full characterization of **4al** in solution; moreover, they showed both that reaction of metalate with MeI was complete within the time of mixing at low temperatures and that the alkylation quantitatively gave **4al**. As described in the Results and Discussion section, increasing the probe temperature allowed the monitoring of the successive transformation of **4al** into **4im** exclusively via the cis isomer of **4al**. When the reaction was complete, the THF solution of **4im** in the 10 mm NMR tube was transferred to a Schlenk tube and reduced to dryness *in vacuo*, giving a dark red solid. Dissolution in light petroleum, followed by filtration and crystallization at −30 °C, afforded **4im** as red crystals. Yield 0.12 g, 73%. Infrared spectra of **4al** were recorded by transferring THF solutions at −30 °C into a precooled solution IR cell immediately prior to recording their spectra.

$Cp^*MoMe(CO)_2(CN\text{-}i\text{-}Pr)$ (4al). Not isolated as a solid; yellow solution at −30 °C. IR (solution in THF, cm^{-1}): 2103 (m, ν_{CN}), 1940 (s), 1872 (s, ν_{CO}). ^1H NMR (300 MHz, −40 °C, THF-d_8): δ −0.36, −0.26 (s, Mo−Me), 1.34 (t_{app}, 2 CHMe_2, ^3J = 6.3 Hz), 1.43 (d, CHMe_2, ^3J = 6.4 Hz), 1.78, 1.82 (s, 2 C_5Me_5), 4.19 (septet, CHMe$_2$, J = 6.3 Hz), 4.34 (septet, CHMe$_2$). $^{13}C\{^1H\}$ NMR (50 MHz, −80 °C, THF-d_8/CD_3OD capillary): δ −12.1, −11.1 (2 Mo−Me), 10.3, 10.4 (2 C_5Me_5), 25.5 (1C, CHMe_2), 26.1 (2C, CHMe_2), 26.3 (1 CHMe_2), 48.8, 49.9 (2 CHMe$_2$), 101.1, 102.2 (2 C_5Me$_5$), 235.4 (2 CO), 241.5, 255.1 (CO), isocyanide Mo−C signals not observed.

$Cp^*Mo(\eta^2\text{-}C(=N\text{-}i\text{-}Pr)Me)(CO)_2$ (4im). Anal. Calcd for $C_{17}H_{25}NO_2Mo$: C, 54.99; H, 6.74; N, 3.77. Found: C, 54.39; H, 6.85; N, 3.41. IR (THF solution, cm^{-1}): 1935 (sh), 1914 (s), 1846 (m), 1812 (s, ν_{CO}), 1693 (m, ν_{CN}). ^1H NMR (200 MHz, 20 °C, C_6D_6): δ 0.63, 0.84 (d, CHMe_2, ^3J = 6.3 Hz), 1.79 (s, C_5Me_5), 2.09 (s, Me), 3.44 (septet, CHMe$_2$). $^{13}C\{^1H\}$ NMR (50 MHz, 20 °C, C_6D_6): δ 7.4 (C_5Me_5), 14.5 (Me), 17.4, 19.7 (CHMe_2), 44.1 (CHMe$_2$), 102.0 (C_5Me$_5$), 195.0 (C═N), 248.0, 251.9 (CO).

Preparation of the η^2-Iminoacyls $CpMo(\eta^2\text{-}C(=N\text{-}t\text{-}Bu)Me)(CO)_2$ (1im), $(MeCp)Mo(\eta^2\text{-}C(=N\text{-}t\text{-}Bu)Me)(CO)_2$ (2im), and $Cp^*Mo(\eta^2\text{-}C(=N\text{-}t\text{-}Bu)Me)(CO)_2$ (3im). The same experimental procedure was employed in the preparation of these compounds; the representative synthesis of $Cp^*Mo(\eta^2\text{-}C(=N\text{-}t\text{-}Bu)Me)(CO)_2$ (**3im**) was as follows.

The parent methyl derivative **3al** (0.5 g, 1.3 mmol) was dissolved in 30 mL of acetone in a Young's ampule, giving a clear yellow-orange solution. The ampule was closed and the contents stirred at 70 °C. Reaction was evidenced by the solution becoming an intense red color. After 2 h at that temperature, the solvent was completely evaporated *in vacuo*, giving a dark red air-sensitive solid. Crystallization from light petroleum ether at −30 °C afforded **3im** as red crystals. Yield 0.32 g, 64%.

$Cp^*Mo(\eta^2\text{-}C(=N\text{-}t\text{-}Bu)Me)(CO)_2$ (3im). Anal. Calcd for $C_{18}H_{27}NO_2Mo$: C, 56.10; H, 7.01; N, 3.64. Found: C, 55.42; H, 7.09; N, 3.41. IR (Nujol mull, cm^{-1}): 1920 (m), 1901 (s), 1822 (m), 1800 (s, ν_{CO}), 1712 (m, ν_{CN}). ^1H NMR (200 MHz, 20 °C, C_6D_6): δ 0.90 (s, CMe_3), 1.79 (s, C_5Me_5), 2.25 (s, Me). $^{13}C\{^1H\}$ NMR (50 MHz, 20 °C, C_6D_6): δ 10.5 (C_5Me_5), 19.4 (Me), 28.3 (CMe_3), 55.9 (CMe$_3$), 104.7 (C_5Me$_5$), 199.2 (C═N), 252.0, 254.8 (CO).

$CpMo(\eta^2\text{-}C(=N\text{-}t\text{-}Bu)Me)(CO)_2$ (1im). Yield 55%. Anal. Calcd for $C_{13}H_{17}NO_2Mo$: C, 49.52; H, 5.40; N, 4.44. Found: C, 49.49; H, 5.56; N, 4.45. IR (Nujol mull, cm^{-1}): 1922 (s), 1816 (s, ν_{CO}), 1711 (m, ν_{CN}). ^1H NMR (200 MHz, 20 °C, C_6D_6): δ 0.82 (s, CMe_3), 2.30 (s, Me), 5.05 (s, C_5H_5). $^{13}C\{^1H\}$ NMR (50 MHz, 20 °C, C_6D_6): δ 20.3 (Me), 27.7 (CMe_3), 55.7 (CMe$_3$), 92.5 (C_5H_5), 189.7 (C═N), 248.8, 251.2 (CO).

$MeCpMo(\eta^2\text{-}C(=N\text{-}t\text{-}Bu)Me)(CO)_2$ (2im). Yield 30%. IR (Nujol mull, cm^{-1}): 1922 (s), 1808 (s, ν_{CO}), 1732 (m, ν_{CN}). ^1H NMR (200 MHz, 20 °C, C_6D_6): δ 0.88 (s, CMe_3), 1.58 (s, MeCp), 2.35 (s, Me), 4.94, 5.07 (br and m, C_5H_4Me). $^{13}C\{^1H\}$ NMR (75 MHz, 20 °C, C_6D_6): δ 14.0 (MeCp), 21.1 (Me), 28.7 (CMe_3), 56.5 (CMe$_3$), 90.4, 92.3, 94.0, 94.7 (CH of MeCp), 111.3 (CMe of MeCp), 192.9 (C═N), 250.0, 252.8 (CO).

Preparation of the η^2-Iminoacyls $CpW(\eta^2\text{-}C(=N\text{-}t\text{-}Bu)Me)(CO)_2$ (5im) and $Cp^*W(\eta^2\text{-}C(=N\text{-}t\text{-}Bu)Me)(CO)_2$ (6im). The same experimental procedure was employed in the preparation of these two compounds; the representative synthesis of $Cp^*W(\eta^2\text{-}C(=N\text{-}t\text{-}Bu)Me)(CO)_2$ (**6im**) was as follows.

The methyl derivative **6al** (0.5 g, 1.1 mmol) was dissolved in 30 mL of CH_3OH in a Young's ampule, giving a clear yellow-orange solution. After the contents were stirred at 70 °C for 30 min, the solution had become an intense red color. NMR experiments showed that production of **6im** had been quantitative. Crystallization from light petroleum ether at −30 °C afforded **6im** as red crystals. Yield 0.35 g, 70%.

$Cp^*W(\eta^2\text{-}C(=N\text{-}t\text{-}Bu)Me)(CO)_2$ (6im). IR (Nujol mull, cm^{-1}): 1917 (s), 1890 (s), 1816 (s), 1784 (s, ν_{CO}),1688 (m, ν_{CN}). ^1H NMR (500 MHz, 20 °C, C_6D_6): δ 0.90 (s, CMe_3), 1.85 (s, C_5Me_5), 2.22 (s, Me). $^{13}C\{^1H\}$ NMR (125 MHz, 20 °C, C_6D_6): δ 11.1 (C_5Me_5), 19.0 (Me), 28.6 (CMe_3), 55.1 (CMe$_3$), 104.3 (C_5-Me$_5$), 195.5 (C═N), 244.1, 248.8 (CO).

$CpW(\eta^2\text{-}C(=N\text{-}t\text{-}Bu)Me)(CO)_2$ (5im). Red crystals. Yield 81%. Anal. Calcd for $C_{13}H_{17}NO_2W$: C, 38.71; H, 4.22; N, 3.47. Found: C, 39.08; H, 4.36; N, 3.39. IR (KBr pellet, cm^{-1}): 1803 (s), 1789 (s, ν_{CO}), 1734 (m, ν_{CN}). ^1H NMR (500 MHz, 20 °C, C_6D_6): δ 0.82 (s, CMe_3), 2.30 (s, Me), 5.11 (s, C_5H_5). $^{13}C\{^1H\}$ NMR (125 MHz, 20 °C, C_6D_6): δ 19.8 (Me), 27.9 (CMe_3), 55.1 (CMe$_3$), 92.2 (C_5H_5), 188.1 (C═N), 242.3, 243.9 (CO).

Thermal Transformation of $CpWMe(CO)_2(CN\text{-}i\text{-}Pr)$ (7al) and $Cp^*WMe(CO)_2(CN\text{-}i\text{-}Pr)$ (8al) in Benzene: Preparation of $CpW(\eta^2\text{-}C(=N\text{-}i\text{-}Pr)Me)(CO)_2$ (7im), $CpW(\eta^3\text{-}CH_2C(H)N\text{-}i\text{-}Pr)(CO)_2$ (7az), $Cp^*W(\eta^2\text{-}C(=N\text{-}i\text{-}Pr)Me)(CO)_2$ (8im), and $Cp^*W(\eta^3\text{-}CH_2C(H)N\text{-}i\text{-}Pr)(CO)_2$ (8az). These two reactions were conducted by following the same experimental procedure; the representative preparation of $Cp^*W(\eta^2\text{-}C(=N\text{-}i\text{-}Pr)Me)(CO)_2$ (**8im**) and $Cp^*W(\eta^3\text{-}CH_2C(H)N\text{-}i\text{-}Pr)(CO)_2$ (**8az**) from $Cp^*WMe(CO)_2(CN\text{-}i\text{-}Pr)$ (**8al**) was as follows.

The parent methyl complex **8al** (1.0 g, 2.2 mmol) was dissolved in 30 mL of C_6H_6 in a Young's ampule, giving a clear, yellow solution. The ampule was sealed, and the solution was stirred at 80 °C; reaction was evidenced by the solution becoming an intense red-brown color. After 2 h at that temperature, the solvent was removed *in vacuo*, leaving an oily red-brown residue. ^1H NMR experiments showed that the residue was comprised of a mixture of **8az** and **8im** only, in the approximate molar ratio 1:1.5 (Note: the corresponding product ratio for the thermolysis of **7al** in benzene was **7az**:**7im** = 2:1). The mixture was redissolved in 20 mL of Et_2O, and separation was effected by chromatography at −30 °C, employing a column of alumina (dimensions 20 × 2 cm) as the static phase and a 5:1 mixture of light petroleum:Et_2O as eluant. **8az** was recovered first as a yellow band, followed by **8im** which provided a red band. Crystallization at −30 °C from light petroleum afforded orange-brown and red crystals of **8az** and **8im** in yields of 25% and 27%, respectively.

Pure **8az** could be isolated from its mixture with **8im** by a second, alternative method. To the aforementioned mixture of **8im** and **8az** in Et_2O was added HBF_4 (2 mL of a commercial 35% w/w solution in H_2O dispersed in 50 mL of Et_2O), which

corresponds to a stoichiometric excess. Addition provoked the immediate precipitation of a yellow solid (presumably the η^3-1-azaallyl salt [Cp*W(η^3-$CH_2C(H)N(H)$−*i*-Pr)$(CO)_2$]BF_4 based on results reported by Green et al.[13b]) from the now clear orange solution. The solution was found to contain (^{1}H NMR) mainly products which appeared to result from the decomposition of **8im**; no attempt to separate or otherwise characterize them was made. The solid azaallyl salt was isolated but not characterized; it did not display sensitivity to air over a 30 min period and readily dissolved in H_2O to give clear yellow solutions. Pure **8az** was generated by suspending the azaallyl salt in 30 mL of Et_2O, to which an excess of a concentrated aqueous NaOH solution was added, effecting the required deprotonation rapidly, the resultant **8az** being taken up by the organic phase. Separation of this phase, drying overnight with anhydrous magnesium sulfate, followed by filtration and crystallization of the product at −30 °C, as described previously, afforded pure **8az**. Yield 32%.

Cp*W(η^2-C(=N-*i*-Pr)Me)$(CO)_2$ (8im). Red crystals. Yield 27%. Anal. Calcd for $C_{17}H_{25}NO_2W$: C, 44.44; H, 5.45; N, 3.05. Found: C, 44.01; H, 5.46; N, 3.09. IR (Nujol mull, cm^{-1}): 1892 (s), 1783 (s, ν_{CO}), 1678 (m, ν_{CN}). ^{1}H NMR (200 MHz, 20 °C, C_6D_6): δ 0.57, 0.82 (d, CH*Me*$_2$, ^3J = 6.4 Hz), 1.85 (s, C_5Me_5), 2.00 (s, Me), 3.23 (septet, C*H*Me_2). ^{13}C{^{1}H} (125 MHz, 20 °C, C_6D_6): δ 11.2 (C_5*Me*$_5$), 17.3 (Me), 21.0, 23.4 (CH*Me*$_2$), 46.6 (*C*HMe_2), 104.7 (C_5Me_5), 195.9 (C=N), 244.9, 249.1 (CO).

Cp*W(η^3-$CH_2C(H)$N-*i*-Pr)$(CO)_2$ (8az). Orange/brown crystals. Yield 25%. Anal. Calcd for $C_{17}H_{25}NO_2W$: C, 44.44; H, 5.45; N, 3.05. Found: C, 44.50; H, 5.41; N, 3.03. IR (Nujol mull, cm^{-1}): 1939 (s), 1861 (s, ν_{CO}). ^{1}H NMR (300 MHz, 20 °C, C_6D_6): δ 0.97 (dd, H_a, $^2J_{as}$ = 0.6, $^3J_{ac}$ = 6.9 Hz), 1.16, 1.17 (d, CH*Me*$_2$, J = 6.4 Hz), 1.69 (s, C_5Me_5), 2.46 (septet, C*H*Me_2), 2.98 (d, H_s, $^3J_{sc}$ = 4.3 Hz), 4.72 (dd, H_c). ^{13}C{^{1}H} NMR (75 MHz, 20 °C, C_6D_6): δ 10.7 (C_5*Me*$_5$), 25.5, 29.2 (CH*Me*$_2$), 32.3 (CH_2), 62.4 (*C*HMe_2), 102.9 (C_5Me_5), 114.3 (CH), 238.5, 238.7 (2 CO).

CpW(η^2-C(=N-*i*-Pr)Me)$(CO)_2$ (7im). Red crystals. Yield 15%. Anal. Calcd for $C_{12}H_{15}NO_2W$: C, 37.02; H, 3.90; N, 3.60. Found: C, 37.94; H, 4.40; N, 3.62. IR (Nujol mull, cm^{-1}): 1890 (s), 1786 (s, ν_{CO}), 1720 (m, ν_{CN}). ^{1}H NMR (200 MHz, 20 °C, C_6D_6): δ 0.53, 0.61 (d, CH*Me*$_2$, ^3J = 6.4 Hz), 2.02 (s, Me), 3.10 (septet, C*H*Me_2), 5.11 (s, C_5H_5). ^{13}C{^{1}H} NMR (50 MHz, 20 °C, C_6D_6): δ 17.3 (Me), 20.2, 21.1 (CH*Me*$_2$), 45.1 (*C*HMe_2), 91.7 (C_5H_5), 246.0, 247.3 (CO), η^2-iminoacyl *C*=N signal not observed.

CpW(η^3-$CH_2C(H)$N-*i*-Pr)$(CO)_2$ (7az). Brown crystals. Yield 42%. Anal. Calcd for $C_{12}H_{15}NO_2W$: C, 37.02; H, 3.90; N, 3.60. Found: C, 37.43; H, 4.11; N, 3.36. IR (Et_2O solution, cm^{-1}): 1948 (s), 1867 (s, ν_{CO}). ^{1}H NMR (200 MHz, 20 °C, C_6D_6): δ 1.08, 1.11 (d, CH*Me*$_2$, ^3J = 6.1 Hz), 2.15 (dd, H_a, $^2J_{as}$ = 1.6, $^3J_{ac}$ = 6.9 Hz), 2.47 (septet, C*H*Me_2), 2.60 (dd, H_s, $^3J_{sc}$ = 4.1 Hz), 4.33 (dd, H_c), 4.87 (s, C_5H_5). ^{13}C{^{1}H} NMR (50 MHz, 20 °C, C_6D_6): δ 20.5 (CH_2), 25.0, 27.8 (CH*Me*$_2$), 60.5 (*C*HMe_2), 92.1 (C_5H_5), 112.5 (CH), 234.3, 235.6 (CO).

Preparation of η^3-1-Azaallyls CpMo(η^3-$CH_2C(H)$N-*t*-Bu)$(CO)_2$ (1az), (MeCp)Mo(η^3-$CH_2C(H)$N-*t*-Bu)$(CO)_2$ (2az), Cp*Mo(η^3-$CH_2C(H)$N-*t*-Bu)$(CO)_2$ (3az), CpW(η^3-$CH_2C(H)$-N-*t*-Bu)$(CO)_2$ (5az), and Cp*W(η^3-$CH_2C(H)$N-*t*-Bu)$(CO)_2$ (6az). The same experimental procedure was employed in the preparations of these compounds; the representative synthesis of Cp*Mo(η^3-$CH_2C(H)$N-*t*-Bu)$(CO)_2$ (**3az**) was as follows.

The parent methyl derivative **3al** (0.5 g, 1.3 mmol) was dissolved in 30 mL of C_6H_6 in a Young's ampule, giving a clear yellow solution. The ampule was sealed and the contents were stirred at 80 °C; reaction was evidenced by the solution darkening to an intense brown color. After 3 h at that temperature, the solvent was evaporated *in vacuo*, giving a dark brown solid. Crystallization from light petroleum ether at −30 °C gave **3az** as brown crystals. Yield 0.4 g, 80%.

The preparations of the W containing complexes **5az** and **6az** were found to require higher temperatures and longer reaction times to drive them to completion, typically 4−5 h at 110 °C.

Cp*Mo(η^3-$CH_2C(H)$N-*t*-Bu)$(CO)_2$ (3az). Anal. Calcd for $C_{18}H_{27}NO_2Mo$: C, 56.10; H, 7.01; N, 3.64. Found: C, 56.29; H, 7.45; N, 3.42. IR (Nujol mull, cm^{-1}): 1946 (s), 1926 (w), 1865 (s), 1828 (w, ν_{CO}). ^{1}H NMR (200 MHz, 20 °C, C_6D_6): δ 0.86 (d, H_a, $^3J_{ac}$ = 7.3 Hz, $^2J_{as}$ not resolved), 1.12 (s, CMe_3), 1.63 (s, C_5Me_5), 2.95 (d, H_s, $^3J_{sc}$ = 4.5 Hz, $^2J_{sa}$ not resolved), 5.09 (dd, H_c). ^{13}C{^{1}H} NMR (50 MHz, 20 °C, C_6D_6): δ 10.1 (C_5*Me*$_5$), 30.8 (C*Me*$_3$), 37.5 (CH_2), 56.6 (*C*Me_3), 104.2 (C_5Me_5), 115.4 (CH), 248.7, 249.4 (CO).

CpMo(η^3-$CH_2C(H)$N-*t*-Bu)$(CO)_2$ (1az). Brown crystals. Yield 49%. Anal. Calcd for $C_{13}H_{17}NO_2Mo$: C, 49.52; H, 5.40; N, 4.44. Found: C, 49.55; H, 5.43; N, 4.28. IR (Nujol mull, cm^{-1}): 1959 (s), 1881 (s, ν_{CO}). ^{1}H NMR (200 MHz, 20 °C, C_6D_6): δ 1.09 (s, CMe_3), 2.16 (d, H_a, $^3J_{ac}$ = 7.4 Hz, $^2J_{as}$ not resolved), 2.52 (d, H_s, $^3J_{sc}$ = 4.1 Hz, $^2J_{sa}$ not resolved), 4.78 (dd, H_c), 4.89 (s, C_5H_5). ^{13}C{^{1}H} NMR (50 MHz, 20 °C, C_6D_6): δ 27.2 (CH_2), 30.7 (C*Me*$_3$), 56.6 (*C*Me_3), 94.7 (C_5H_5), 115.0 (CH), 247.4, 247.7 (CO).

(MeCp)Mo(η^3-$CH_2C(H)$N-*t*-Bu)$(CO)_2$ (2az). Brown crystals. Yield 35%. IR (Nujol mull, cm^{-1}): 1946 (s), 1864 (s, ν_{CO}). ^{1}H NMR (200 MHz, 20 °C, C_6D_6): δ 1.08 (s, CMe_3), 1.40 (s, *Me*Cp), 1.76 (dd, H_a, $^2J_{as}$ = 0.8, $^3J_{ac}$ = 7.3 Hz), 2.63 (dd, H_s, $^3J_{sc}$ = 3.6 Hz), 4.63, 4.75, 4.88 (m, C_5H_4Me), 4.93 (dd, H_c). ^{13}C-{^{1}H} NMR (50 MHz, 20 °C, C_6D_6): δ 13.0 (*Me*Cp), 29.3 (CH_2), 31.0 (C*Me*$_3$), 56.9 (*C*Me_3), 88.9, 89.7, 92.8, 94.7, 97.5 (C_5H_4-Me), 114.9 (CH), 247.5, 247.6 (CO).

CpW(η^3-$CH_2C(H)$N-*t*-Bu)$(CO)_2$ (5az). Brown crystals. Yield 72%. Anal. Calcd for $C_{13}H_{17}NO_2W$: C, 38.71; H, 4.22; N, 3.47. Found: C, 39.55; H, 4.28; N, 2.86. IR (KBr pellet, cm^{-1}): 1920 (s), 1830 (s, ν_{CO}). ^{1}H NMR (200 MHz, 20 °C, C_6D_6): δ 1.04 (s, CMe_3), 2.22 (dd, H_a, $^2J_{as}$ = 1.4, $^3J_{ac}$ = 6.6 Hz), 2.61 (dd, H_s, $^3J_{sc}$ = 4.2 Hz), 4.63 (dd, H_c), 4.89 (s, C_5H_5). ^{13}C{^{1}H} NMR (50 MHz, 20 °C, C_6D_6): δ 18.4 (CH_2), 29.9 (C*Me*$_3$), 56.5 (*C*Me_3), 92.8 (C_5H_5), 111.8 (CH), 236.9, 237.0 (CO).

Cp*W(η^3-$CH_2C(H)$N-*t*-Bu)$(CO)_2$ (6az). Brown crystals. Yield 65%. Anal. Calcd for $C_{18}H_{27}NO_2W$: C, 45.67; H, 5.71; N, 2.96. Found: C, 45.04; H, 5.59; N, 2.45. IR (Nujol mull, cm^{-1}): 1930 (s), 1846 (s, ν_{CO}). ^{1}H NMR (500 MHz, 20 °C, C_6D_6): δ 0.94 (dd, H_a, $^2J_{as}$ = 1.0, $^3J_{ac}$ = 6.5 Hz), 1.10 (s, CMe_3), 1.69 (s, C_5Me_5), 2.98 (dd, H_s, $^3J_{sc}$ = 4.3 Hz), 5.00 (dd, H_c). ^{13}C{^{1}H} NMR (125 MHz, 20 °C, C_6D_6): δ 11.1 (C_5*Me*$_5$), 16.9 (CH_2), 31.5 (C*Me*$_3$), 57.9 (*C*Me_3), 103.4 (C_5Me_5), 113.1 (CH), 239.7, 241.3 (CO).

Preparation of the Heterometallacycles Cp*W(η^2(*C,O*)-C(Me)N(*i*-Pr)C(Me)$_2$O)$(CO)_2$ (8cad), CpW(η^2(*C,O*)-C(Me)N-(Me)C(Me)$_2$O)$(CO)_2$ (9cad), and Cp*W(η^2(*C,O*)-C(Me)N-(Et)CH(Me)O)$(CO)_2$ (10cad). The same experimental procedure was followed in the preparations of **8cad**, **9cad**, and **10cad** (acetaldehyde in place of acetone); the representative synthesis of Cp*W(η^2(*C,O*)-C(Me)N(*i*-Pr)C(Me)$_2$O)$(CO)_2$ (**8cad**) was as follows.

The parent complex **8al** (1.0 g, 2.2 mmol) was dissolved in 30 mL of acetone in a Young's ampule producing a clear, yellow solution. This solution was then stirred at 40 °C for 12 h resulting in the color becoming an intense orange. Solvent was removed *in vacuo*, and the oily product mixture was redissolved in 20 mL of Et_2O. Separation was effected by chromatography at −30 °C, as described in the procedure for the isolation of **8az** and **8im**. The latter two compounds eluted first by employing a 5:1 mixture of light petroleum:Et_2O, and the product **8cad** remained at the upper part of the column as an orange band. Elution with pure Et_2O rapidly removed **8cad** from the column; evaporation of solvent followed by crystallization from Et_2O at −30 °C afforded **8cad** as moderately air-sensitive orange crystals. Yield 0.42 g, 37%.

Cp*W(η^2(*C,O*)-C(Me)N(*i*-Pr)C(Me)$_2$O)$(CO)_2$ (8cad). Anal. Calcd for $C_{20}H_{31}NO_3W$: C, 46.42; H, 6.00; N, 2.71. Found: C, 45.95; H, 6.13; N, 2.86. IR (KBr pellet, cm^{-1}): 1892 (s), 1800 (s, ν_{CO}). ^{1}H NMR (200 MHz, 20 °C, C_6D_6): δ 0.85 (d, CH*Me*$_2$, ^3J = 7.0 Hz), 1.17 (br s, $OCMe_2$), 1.78 (s, C_5Me_5), 2.69 (s, NCMe), 3.27 (septet, C*H*Me_2), ^{1}H NMR (300 MHz, −30 °C, C_7D_8): δ 0.77, 0.82 (d, CH*Me*$_2$, ^3J = 7.0 Hz), 1.06, 1.29 (s, $OCMe_2$), 1.80 (s, C_5Me_5), 2.66 (s, NCMe), 3.05 (septet, C*H*Me_2).

$^{13}C\{^1H\}$ NMR (75 MHz, 40 °C, C_7D_8): δ 10.2 (C_5Me_5), 21.4 ($CHMe_2$), 33.2 ($NCMe$), 51.1 ($CHMe_2$), 104.1 (C_5Me_5), 109.3 ($OCMe_2$), 251.8 (C═N), methyl signals of incorporated acetone fragment and carbonyl resonances not observed due to fluxionality. ^{13}C $\{^1H\}$NMR (75 MHz, −30 °C, C_7D_8): δ 10.6 (5 C_5Me_5), 20.7, 21.5 ($CHMe_2$), 23.5, 31.6 ($OCMe_2$), 33.5 ($NCMe$), 51.3 ($CHMe_2$), 104.2 (C_5Me_5), 109.3 ($OCMe_2$), 248.0 (CO), 250.9 (C═N), 265.3 (CO).

CpW(η^2(*C,O*)-C(Me)N(Me)C(Me)$_2$O)(CO)$_2$ (9cad). Orange/red crystals. Yield 54%. Anal. Calcd for $C_{13}H_{17}NO_3W$: C, 37.23; H, 4.06; N, 3.34. Found: C, 37.85; H, 3.92; N, 3.41. IR (KBr pellet, cm^{-1}): 1908 (s), 1816 (s, ν_{CO}). ^1H NMR (300 MHz, 20 °C, C_7D_8): δ 1.01 (br s, $OCMe_2$), 2.27 (s, MeNC), 2.40 (s, NCMe), 5.13 (s, C_5H_5). ^1H NMR (300 MHz, −30 °C, C_7D_8): δ 0.99, 1.09 (s, $OCMe_2$), 2.15 (s, MeNC), 2.35 (s, NCMe), 5.13 (s, C_5H_5). $^{13}C\{^1H\}$ NMR (75 MHz, 20 °C, C_7D_8): δ 24.0, 28.2 (broad resonances, $OCMe_2$), 33.3 ($NCMe$), 34.1 ($CNMe$), 94.1 (C_5H_5), 108.0 ($OCMe_2$), 243.4 (CO), 247.1 (C═N), 259.2 (CO).

Cp*W(η^2(*C,O*)-C(Me)N(Et)CH(Me)O)(CO)$_2$ (10cad). Orange crystals. Yield 32%. IR (Nujol mull, cm^{-1}): 1908 (s), 1812 (s, υ_{CO}), 1527 (m), 1385 (m). ^1H NMR (500 MHz, 20 °C, C_7D_8): δ 0.64 (t, CH_2Me, ^3J = 7.2 Hz), 1.05 (br s, $OCHMe$), 1.79 (s, C_5Me_5), 2.37 (s, NCMe), 2.65, 2.75 (broad singlets, CH_2-Me), 5.5 (br s, $OCHMe$). $^{13}C\{^1H\}$ NMR (125 MHz, 20 °C, C_7D_8): δ 10.6 (C_5Me_5), 14.4 (CH_2Me), 30.8 ($NCMe$), 39.7 (broad resonance, CH_2Me), 101.6 (C_5Me_5), 104.4 ($OCHMe$), 224.8 (broad resonance, CO), 250.1 (broad resonance, CN), 263.2 (broad resonance, CO).

Study of the Transformation of the Methyl Derivative 3al into the Isomeric η^2-Iminoacyl 3im and η^3-1-Azaallyl 3az by Mild Thermolysis in a Range of Solvents of Different Donor Ability. The complex **3al** (0.03 g, 0.08 mmol) was dissolved in 20 mL of an appropriate solvent in a Young's ampule. The solution was then stirred at 80 °C for 3 h, resulting in a color change from the clear yellow of the starting material to that of the product(s). When the reaction was complete, the solvent was removed *in vacuo* and the contents were redissolved in 0.5 mL of C_6D_6. Integration of the Cp* singlets in the ^1H NMR spectra allowed the calculation of the molar ratio of products **3az**:**3im**, expressed as percentages in Table 3. Moreover, these experiments confirmed that the mild thermolysis of **3al** cleanly generates **3im** and **3az** as the only products detected by NMR. No evidence for the interconversion of **3im** and **3az** was obtained at this reaction temperature.

X-ray Structure Determination of Compound 1az. A summary of the fundamental crystal data is given in Table 1. A brown crystal of prismatic shape was resin epoxy-coated and mounted in a κ diffractometer. The cell dimensions were refined by least-squares fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo were taken from the *International Tables for X-Ray Crystallography*.[32] The structure was solved by Patterson and Fourier methods. An empirical absorption correction[33] was applied at the end of the isotropic refinement. A final refinement was undertaken with fixed isotropic factors and coordinates for H atoms. Most of the calculations were carried out with the *X-Ray 80 system*.[34]

X-ray Structure Determination of Compounds 9cad. Crystal data, structure solution, and refinement details are summarized in Table 1. A red prism crystal with dimensions *ca.* 0.30 × 0.22 × 0.53 mm was mounted, in air, on a glass fiber and transferred to a MSC-Rigaku AFC6S diffractometer (with graphite monochromated Mo Kα radiation) where accurate cell parameters were refined from the settings of 25 reflections in the range 11.33° < 2θ < 17.08°. During processing, corrections were applied for Lorentz and polarization effects, crystal deterioration (5% overall from the intesities of three standard reflections measured every 200), and absorption (empirically determined). The independent reflections (2011) were entered into the TEXSAN system[35] for structure determination by the heavy-atom method (for the W atom) and phase-expansion and -refinement for the remainder of the structure. Refinement of the structural model was by full-matrix least-squares methods. The non-hydrogen atoms were refined anisotropically. Approximately half of the hydrogen atoms were localized in difference Fourier maps, and the remainder were included in idealized positions, they were not refined. The refinement was terminated with R = 0.029 and R_w = 0.036 for 1562 reflections with I > 3σ(*I*), weighted $w = \sigma(F)^{-2}$. Scattering curves for neutral atoms were taken from those included in the TEXSAN system, which was running on a DEC VAX 3520 computer at the Servicios Centralizados de Ciencia y Tecnología de la Universidad de Cádiz.

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Supporting Information Available: Crystallographic tables for **1az** and **9cad** including positional and thermal parameters, fractional coordinates, and bond lengths and angles (13 pages). Ordering information is given on any current masthead page.

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