Thermal Conversion of η^2-Acyl−Isocyanide Complexes into Isomeric η^2-Iminoacyl−Carbonyl Derivatives

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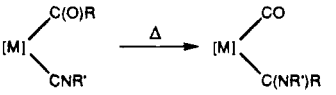
Abstract: The η^2-acyl−isocyanide complexes Bp′Mo(η^2-C(O)R)(CN-*t*-Bu)CO(PMe$_3$) have been prepared from the known acyls Mo(η^2-C(O)R)Cl(CO)(PMe$_3$)$_3$ by a two-step procedure that involves treatment with the bidentate monoanionic ligand Bp′ (Bp′ = unsubstituted and 3,5-Me$_2$-substituted dihydrobis(pyrazolyl)borate, Bp and Bp*, respectively) followed by PMe$_3$ substitution by CN-*t*-Bu. These compounds undergo irreversible, thermal isomerization (10−70 °C) to the corresponding η^2-iminoacyl−carbonyl derivatives Bp′Mo(η^2-C(N-*t*-Bu)R)(CO)$_2$(PMe$_3$), thereby demonstrating the greater thermodynamic stability of the latter compounds. This isomerization reaction follows first-order kinetics, and it is characterized by activation parameters $\Delta H^{\ddagger} = 20.3 \pm 1.4$ kcal·mol^{-1} and $\Delta S^{\ddagger} = -12.6 \pm 1.2$ cal·mol^{-1}·K^{-1}. A pair of complexes implicated in this acyl−isocyanide to iminoacyl−carbonyl isomerization, namely the CH$_2$SiMe$_3$ derivatives Bp*Mo(η^2-C(O)CH$_2$SiMe$_3$)(CN-*t*-Bu)(CO)(PMe$_3$) (**4b**) and Bp*Mo(η^2-C(N-*t*-Bu)CH$_2$SiMe$_3$)(CO)$_2$(PMe$_3$) (**6b**), have been structurally characterized by single-crystal X-ray determinations.

Carbon monoxide and organic isocyanides are isoelectronic molecules with similar bonding capabilities, the latter being generally considered better σ-donors and somewhat less efficient π-acceptors than the former.[1] The insertion of CO into a transition metal−carbon bond is a fundamental organometallic reaction, often proposed as an important intermediate step in several catalytic processes.[1] The analogous insertion of isocyanides is also a commonly observed transformation. Both processes have been the subject of numerous synthetic and mechanistic investigations that have disclosed their similarities and peculiarities.[2]

Extended Hückel molecular orbital studies of the reaction path for these insertions[3] suggest that iminoacyls are in general thermodynamically more stable than their acyl counterparts, although kinetically, the activation barrier seems to be higher for CNR insertion. From this theoretical picture, an experimental situation emerges where competition reactions involving CO or CNR insertion are expected to lead to the iminoacyl products. Indeed, a number of cases reported in the literature are in accord with this expectation,[4] but the situation is far from clear and there are also other apparently conflicting reports in which acyl formation is the sole reaction detected.[5] In addition,

Scheme 1



a mixture of the two types of the complex has been obtained in some instances such as in the interaction of the anionic species [Tp′Mo(CO)$_2$(CN-*t*-Bu)]$^-$ with MeI[6] (Tp′ = hydrotris(pyrazolyl)borate ligand). Moreover, it has recently been reported that the observation of one reaction or the other, i.e. the CO or the CNR insertion, depends strongly upon the nature of the isocyanide and the facility of insertion varying in the order aromatic isocyanide > CO > aliphatic isocyanide.[7]

A perusal of the literature data therefore suggests that iminoacyls are the thermodynamic products of these reactions and consequently that CO insertion may be imposed on kinetic grounds. Nonetheless, no unequivocal experimental demonstration of this hypothesis seems to have been provided, and to our knowledge, the very important isomerization depicted in Scheme 1 has never been demonstrated.[8a]

Although a major goal in our long-standing interest in the chemistry of acyl and iminoacyl complexes of the transition

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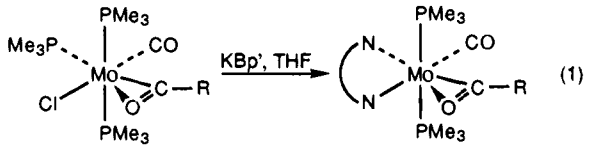
metals[9] has been the fulfillment of the above transformation,[8c] it is only recently that we have succeeded in finding a suitable system. Herein, we report the results of this research undertaking, which comprise the synthesis and structural characterization (including single-crystal X-ray studies for two selected compounds) of isomeric Bp′Mo(η^2-C(O)R)(CNR′)(CO)(PMe_3) complexes **3** and **4** and isomeric Bp′Mo(η^2-C(N-*t*-Bu)R)$(CO)_2$-(PMe_3) complexes **5** and **6** (Bp′ = $H_2B(pz)_2$, Bp; $H_2B(3,5\text{-}Me_2pz)_2$, Bp*). A kinetic investigation of an example of this isomerization is also reported.

Results and Discussion

Treatment of tetrahydrofuran (THF) solutions of the known acyls Mo(η^2-C(O)R)Cl(CO)$(PMe_3)_3$[9b] with the potassium salt of the bidentate N-donors, dihydrobis(pyrazolyl)borate ligands,[10] KBp′ affords high yields of complexes **1** and **2**, according to eq 1.[11] With the exception of **1b**, which is obtained as a



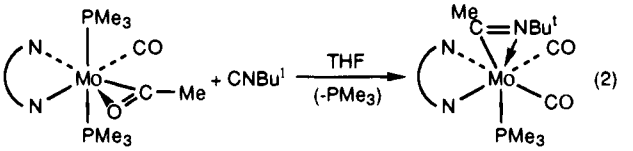
(1)

Bp, R = Me, **1a**; CH_2SiMe_3, **1b**; CH_2CMe_3, **1c**

Bp*, R = Me, **2a**; CH_2SiMe_3, **2b**; CH_2CMe_3, **2c**

spectroscopically pure oil, the new acyls are red-orange crystalline solids. They are freely soluble in common organic solvents in which they give air-sensitive solutions. Complexes **2a** and **2c** are thermally unstable and decompose quickly to complex mixtures of products in the absence of added PMe_3. The Mo–η^2-acyl linkage is characterized by an IR absorption in the proximity of 1500 cm^{-1} and by a ^{13}C resonance at 270 ppm. This shows coupling to the two ^{31}P nuclei and, upon gate decoupling, to the adjacent methyl or methylene protons (see Experimental Section). The trans disposition of the PMe_3 ligands is denoted by the observation of virtually coupled triplets[12] both in the ^1H and in the $^{13}C\{^1H\}$ NMR spectra. In accord with the behavior found for other related derivatives, compounds **1** and **2** are fluxional in solution, their dynamic behavior being associated with a librational motion of the acyl ligand.[13]

The addition of 1 equiv of CN-*t*-Bu to THF solutions of Bp–Me derivative **2a** cooled at −30 °C causes no observable reaction, but upon the solutions being warmed to room temperature a smooth transformation ensues that gives iminoacyl **5a** (eq 2). No intermediates can be detected. Complex **5a** has

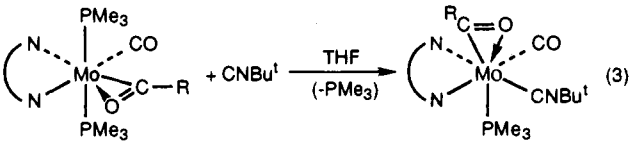


(2)

2a **5a**

been fully characterized by analytical and spectroscopic data (see below). The thermal stability of this compound with respect to its conversion into the unobserved, isomeric acyl–isocyanide, BpMo(η^2-C(O)Me)(CN-*t*-Bu)(CO)(PMe_3), unambiguously indicates that it is the thermodynamic product of the above reaction. However, the lability of this purported intermediate with respect to isocyanide insertion does not permit its detection, and therefore, the transformation depicted in Scheme 1 cannot be observed.

An increase of the steric requirements of the Bp′ ligand and the alkyl group allows for isolation of the desired acyl–isocyanide complexes **3** and **4** (eq 3). For the unsubstituted

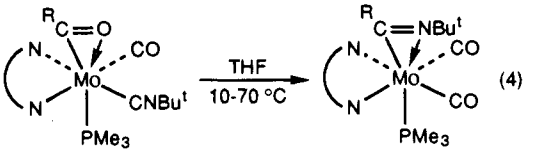


(3)

1, 2 Bp, **3c**; Bp*, **4a-4c**

Bp ligand only the bulkiest CH_2CMe_3 alkyl affords an isolable acyl–isocyanide, **3c**, while for the more sterically demanding Bp*, the three alkyl groups investigated provide stable derivatives, **4a–4c**. These alkyl–isocyanides are characterized by MCO and MCN-*t*-Bu absorptions at ca. 1800 and 2060 cm^{-1}, respectively, and by a medium-intensity band at ca. 1560 cm^{-1} due to the acyl moiety. Additional support for the proposed formulation comes from spectroscopic studies and from a single-crystal X-ray investigation of complex **4b** (see following section).

Thermal isomerization of acyl–isocyanides **3** and **4** to corresponding iminoacyl–carbonyls **5** and **6** occurs upon heating THF solutions of the former complexes (eq 4). The reactions



(4)

3, 4 Bp, **5**; Bp*, **6**

are essentially complete in 1–2 h; further heating of the solutions does not induce any additional change. This unambiguously demonstrates that, at least in this system, the iminoacyl–carbonyl isomer is thermodynamically more stable than the acyl–isocyanide formulation. The structure proposed

(8) In some cases, the acyl → iminoacyl conversion has been proposed. The corresponding reactions are, however, complex and require the use of an excess of CNR and dissociation or, alternatively, coupling of the iminoacyl with other coordinated ligands. Direct comparison of the two isomeric structures is, therefore, not feasible. See: (a) Bellachioma, G.; Cardaci, G.; Zanazzi, P. *Inorg. Chem.* **1987**, *26*, 84. (b) Motz, P. L.; Williams, J. P.; Alexander, J. J.; Ho, D. M. *Organometallics* **1989**, *8*, 1523. (c) It should be noted that the transformation of Scheme 1 is a particular, simpler variation of the more general reaction [M]C(O)R + CNR′ → [M]C-(NR′)R + CO. To our knowledge, this conversion has not been observed either.

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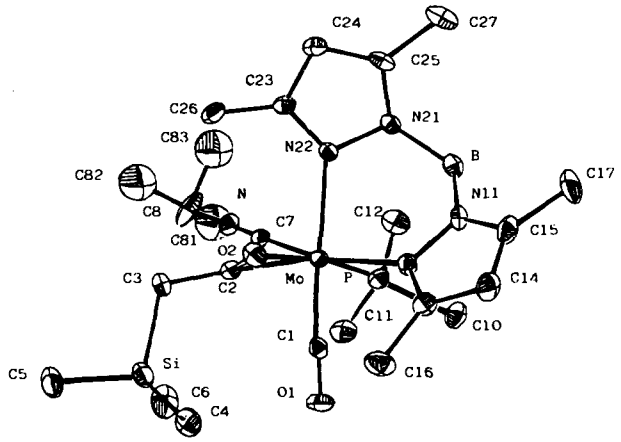


Figure 1. ORTEP diagram of Bp*Mo(η^2-C(O)CH_2SiMe_3)(CN-*t*-Bu)-(CO)(PMe_3) (**4b**).

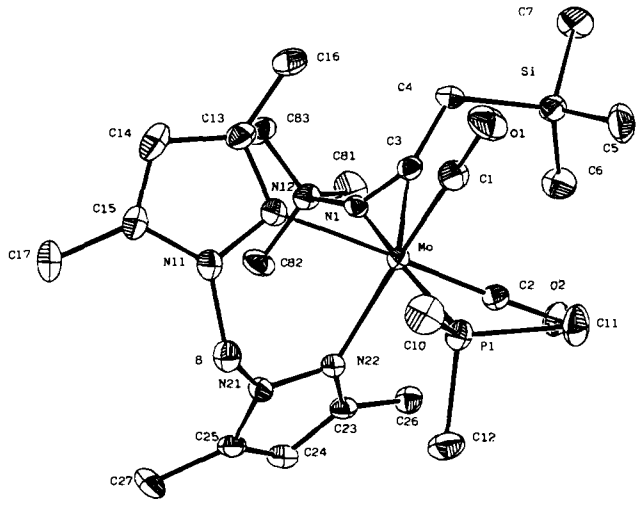


Figure 2. ORTEP diagram of Bp*Mo(η^2-C(N-*t*-Bu)CH_2SiMe_3)$(CO)_2$-(PMe_3) (**6b**).

for these complexes is based on the following spectroscopic observations: (i) two IR absorptions at ca. 1925 and 1800 cm^{-1} and a $^{13}C\{^1H\}$ NMR resonance in the proximity of 240 ppm due to the terminal carbonyl ligands and (ii) an IR band at ca. 1725 cm^{-1} together with a $^{13}C\{^1H\}$ signal at ca. 200 ppm associated with the Mo–η^2-iminoacyl entity. Both are in the region expected for dihaptoiminoacyl ligands bonded to early transition metals[2e,9] and can therefore be taken as strong evidence in support of this binding mode. A structural determination of compound **6b** (see following section) by X-ray techniques confirms this proposal.

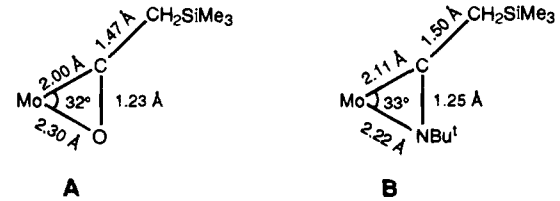
Solid-State Structures of Complexes 4b and 6b. Although analytical and spectroscopic data are fully in accord with the formulation proposed for acyl and iminoacyl derivatives **3**–**6**, we considered it appropriate to characterize a pair of complexes implicated in the acyl–isocyanide → iminoacyl–carbonyl isomerization of Scheme 1 by X-ray methods. Compounds **4b** and **6b** readily provide single crystals suitable for X-ray studies and were therefore chosen for this investigation.

The molecular structures of isomers **4b** and **6b** are presented in Figures 1 and 2, which also include the atom numbering scheme. Tables 1 and 2 collect important bond distances and angles, while in Table 3 a summary of crystallographic data for both compounds is recorded. The small bite angles of the η^2-acyl and η^2-iminoacyl ligands justify consideration of these fragments as occupants of a single coordination site. Accordingly, complexes **4b** and **6b** can be regarded as having a

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **4b**

MO–P	2.479(3)	N21–N22	1.384(8)
MO–N12	2.252(6)	N21–C25	1.341(9)
MO–N22	2.298(6)	N21–B	1.547(12)
MO–C1	1.910(8)	N22–C23	1.335(10)
MO–O2	2.302(6)	C23–C24	1.381(10)
MO–C2	1.994(8)	C23–C26	1.487(12)
MO–C7	2.044(8)	C24–C25	1.356(12)
P–C10	1.826(9)	C25–C27	1.504(12)
P–C11	1.814(9)	C1–O1	1.172(9)
P–C12	1.798(9)	O2–C2	1.230(9)
N11–N12	1.386(8)	C2–C3	1.477(11)
N11–C15	1.347(10)	C3–SI	1.929(9)
N11–B	1.540(12)	SI–C4	1.828(11)
N12–C13	1.321(9)	SI–C5	1.830(11)
C13–C14	1.377(120	SI–C6	1.861(11)
C13–C16	1.509(12)	C7–N1	1.159(10)
C14–C15	1.391(12)	N1–C8	1.457(12)
C15–C17	1.488(13)		
C2–MO–C7	77.7(3)	N12–MO–C2	114.5(3)
O2–MO–C7	105.9(3)	N12–MO–O2	84.0(2)
O2–MO–C2	32.3(3)	N12–MO–C1	90.8(3)
C1–MO–C7	99.4(3)	N12–MO–N22	83.6(2)
C1–MO–C2	84.1(3)	P–MO–C7	74.7(2)
C1–MO–O2	94.7(3)	P–MO–C2	143.2(3)
N22–MO–C7	86.4(3)	P–MO–O2	171.6(2)
N22–MO–C2	97.0(3)	P–MO–C1	77.0(2)
N22–MO–O2	83.4(2)	P–MO–N22	105.0(2)
N22–MO–C1	174.2(3)	P–MO–N12	97.2(2)
N12–MO–C7	165.0(7)		

distorted octahedral structure. The ligand arrangement is such that it leaves the N atoms of the Bp* ligands and the two π-acceptor groups (CO or CO and CN-*t*-Bu) in the equatorial plane and the acyl or iminoacyl moiety in an axial position trans to the phosphine. The Mo–η^2-acyl and –η^2-iminoacyl linkages (**A** and **B**, respectively) are characterized by relatively short



Mo–C and Mo–X (X = O, N-*t*-Bu) contacts (e.g. Mo–C bond lengths of 1.994(8) and 2.115(8) Å, respectively, for **4b** and **6b**) similar to those found in other η^2-acyl and η^2-iminoacyl complexes of Mo(II).[9,13,14] Other bond lengths and angles also have normal values and need no further comment.

Kinetics of the 3c → 5c Isomerization. A comparative study of the velocity of the acyl–isocyanide → iminoacyl–carbonyl isomerization shows a strong dependence on the size of the alkyl group and the bis(pyrazolyl)borate ligand. The rate of the reaction increases in the order CH_2CMe_3 < CH_2SiMe_3 < Me and Bp* < Bp. Hence, the fastest isomerization corresponds to the least sterically demanding set of R and Bp′ fragments, i.e. Me and Bp, while for the considerably bulkier combination of CH_2CMe_3 and Bp* groups, the isomerization is so slow that a competitive reaction leading to the hydroboration of the η^2-acyl fragment occurs preferentially.[15]

Neopentyl–Bp complex **3c** is thermally stable under ambient conditions but converts into iminoacyl isomer **5c** at higher temperatures at a rate that can be conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The reaction exhibits clean, first-order kinetics over at least 3–4 half-lives. From the rates

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **6b**

MO−P1	2.481(2)	MO′−P1′	2.476(2)
MO−N12	2.307(7)	MO′−N12′	2.318(6)
MO−N22	2.254(6)	MO′−N22′	2.266(6)
MO−C1	1.946(8)	MO′−C1′	1.905(7)
MO−C2	1.914(9)	MO′−C2′	1.914(9)
MO−N1	2.220(6)	MO′−N1′	2.223(6)
MO−C3	2.115(8)	MO′−C3′	2.119(8)
N11−B1	1.53(1)	N11′−B′	1.53(1)
N21−B1	1.53(1)	N21′−B′	1.53(1)
C1−O1	1.17(1)	C1′−O1′	1.182(9)
C2−O2	1.18(1)	C2′−O2′	1.18(1)
N1−C3	1.253(9)	N1′−C3′	1.248(9)
N1−C8	1.476(9)	N1′−C8′	1.49(1)
C3−C4	1.50(1)	C3′−C4′	1.49(1)
C4−SI	1.893(9)	C4′−SI′	1.907(8)
SI−C5	1.82(1)	SI′−C5′	1.83(1)
SI−C6	1.83(1)	SI′−C6′	1.83(1)
SI−C7	1.84(1)	SI′−C7′	1.83(1)
C8−C81	1.50(1)	C8′−C81′	1.50(1)
C8−C82	1.52(1)	C8′−C82′	1.50(1)
C8−C83	1.50(1)	C8′−C83′	1.50(1)
N1−MO−C3	33.5(3)	N1′−MO′−C3′	33.3(3)
C2−MO−C3	86.0(3)	C2′−MO′−C3′	76.2(4)
C2−MO−N1	95.9(3)	C2′−MO′−N1′	107.3(3)
C1−MO−C3	76.3(3)	C1′−MO′−C3′	85.4(3)
C1−MO−N1	107.7(3)	C1′−MO′−N1′	94.7(3)
C1−MO−C2	92.7(4)	C1′−MO′−C2′	94.0(4)
N22−MO−C3	119.9(3)	N22′−MO′−C3′	119.8(3)
N22−MO−N1	87.6(2)	N22′−MO′−N1′	87.5(2)
N22−MO−C2	92.0(3)	N22′−MO′−C2′	163.3(3)
N22−MO−C1	163.4(3)	N22′−MO′−C1′	92.5(3)
N12−MO−C3	93.9(3)	N12′−MO′−C3′	93.4(3)
N12−MO−N1	83.4(2)	N12′−MO′−N1′	83.2(2)
N12−MO−C2	178.8(3)	N12′−MO′−C2′	87.8(3)
N12−MO−C1	88.4(3)	N12′−MO′−C1′	177.6(3)
N12−MO−N22	87.0(2)	N12′−MO′−N22′	86.3(2)
P1−MO−C3	147.0(2)	P1′−MO′−C3′	147.1(3)
P1−MO−N1	173.8(2)	P1′−MO′−N1′	174.1(2)
P1−MO−C2	78.5(3)	P1′−MO′−C2′	75.7(3)
P1−MO−C1	75.5(3)	P1′−MO′−C1′	79.9(3)
P1−MO−N22	89.9(2)	P1′−MO′−N22′	90.3(2)
P1−MO−N12	102.1(2)	P1′−MO′−N12′	102.2(2)
MO−C1−O1	178.1(8)	MO′−C1′−O1′	176.9(7)
MO−C2−O2	177.4(7)	MO′−C2′−O2′	178.5(8)
MO−N1−C8	155.6(5)	MO′−N1′−C8′	155.2(5)
MO−N1−C3	68.6(4)	MO′−N1′−C3′	68.8(5)
C3−N1−C8	134.9(7)	C3′−N1′−C8′	134.9(7)
N1−C3−C4	136.0(7)	N1′−C3′−C4′	137.1(8)
MO−C3−C4	146.0(6)	MO′−C3′−C4′	145.0(6)

Table 3. Crystal and Refinement Data for **4b** and **6b**

	4b	6b
formula	$MoPSiO_2N_5C_{24}BH_{45}$	$MoPSiO_2N_5C_{24}BH_{45}$
M_r	601.5	601.5
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
a, Å	10.772(2)	38.87(2)
b, Å	16.630(2)	9.606(4)
c, Å	18.335(4)	17.211(4)
β	97.13(2)	103.31(2)
V, Å^3	3259(4)	6254(4)
Z	4	8
$F(000)$	1264	2528
d_{calcd}, g cm^{-3}	1.23	1.27
temp, °C	22	22
μ(Mo Kα)	5.01	5.23
cryst dimens, mm	0.4 × 0.2 × 0.2	0.3 × 0.2 × 0.4
diffractometer	Enraf−Nonius CAD4	Enraf−Nonius CAD4
radiation	graphite-monochromated Mo Kα (λ = 0.710 69 Å)	graphite-monochromated Mo Kα (λ = 0.710 69 Å)
scan technique	$\Omega/2\theta$	$\Omega/2\theta$
θ	$1 < \theta < 28$	$1 < \theta < 25$
data collected	(−14,0,0) to (14,22,24)	(−46,0,0) to (46,11,20)
unique data	7803	5520
unique data ($I \geq 2\sigma(I)$)	3634	4506
R(int), %	0.9	0.7
std rflns	3/172 rflns	3/170 rflns
R	0.062	0.032
R_w	0.064	0.036
average shift/error	0.05	0.3

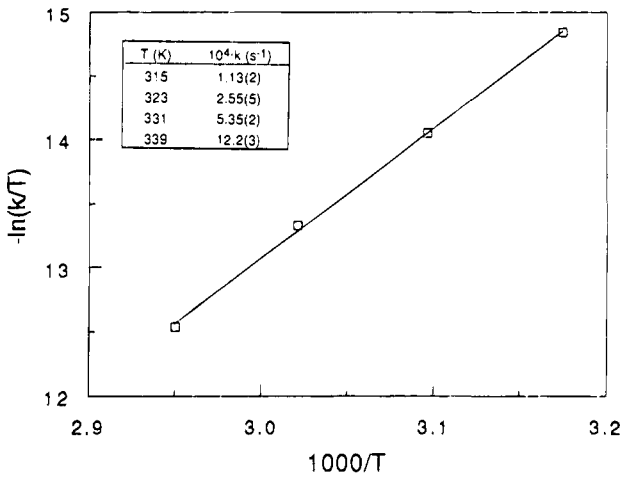
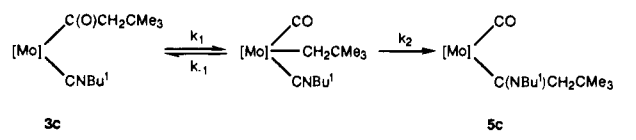


Figure 3. Plot of $-\ln(k/T)$ vs $1000/T$ for the thermal conversion of **3c** into **5c** in toluene at four temperatures between 42 and 66 °C.

Scheme 2



determined at four different temperatures in the range 42−66 °C, the values of 20.3 ± 1.4 kcal·mol^{-1} and −12.6 ± 1.2 cal·mol^{-1}·K^{-1} can be computed for the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively (Figure 3).

Although a detailed investigation of the course of this reaction has not been undertaken, some useful mechanistic comments can be made at this point. A plausible, albeit somewhat simplified,[16] mechanism is presented in Scheme 2. Note that, in accord with literature data, isocyanide insertion has been postulated as irreversible.[17]

Two possibilities can be considered: (i) rate-determining isocyanide insertion is preceded by a fast pre-equilibrium between **3c** and the alkyl intermediate or (ii) deinsertion of **3c** is the slow step and it is followed by fast isocyanide insertion. Since, as already pointed out, the observed trend for isomerization is Bp* < Bp and CH_2CMe_3 < CH_2SiMe_3 < Me,[18,19] it seems plausible that the formation of the sterically congested seven-coordinate alkyl−carbonyl−isocyanide intermediate oc-

(16) Doubtless, $\eta^2 \rightleftharpoons \eta^1$ acyl and iminoacyl interconversions must take place during the isomerization reaction. They are, however, expected to be very fast[9] and, therefore, to have no influence on the overall kinetics. For the sake of simplicity, the coordination mode of the acyl and iminoacyl ligand has not been specified in Scheme 2.

(17) While there is a wealth of information about the reversibility of CO insertion into M−C bonds, the analogous reaction of isocyanides is usually an irreversible process. Some rather unusual examples have been reported, however. See: (a) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 2665. (b) Cámpora, J.; Gutiérrez, E.; Monge, A.; Poveda, M. L.; Ruiz, C.; Carmona, E. *Organometallics* **1993**, *12*, 4025. (c) Bellachioma, G.; Cardaci, G.; Zanazzi, P. *Inorg. Chem.* **1987**, *26*, 84. (d) Bellachioma, G.; Cardaci, G.; Macchioni, A,; Reichenbach, G. *Gazz. Chim. Ital.* **1991**, *121*, 101. (e) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G. *Inorg. Chem.* **1992**, *31*, 63.

(18) This order is the opposite of the normal sequence found for insertion reactions,[1b,19] CH_2CMe_3 > CH_2SiMe_3 > Me.

curs in the rate-determining step, which is subsequently followed by fast, irreversible rearrangement to product **5c**.

Conclusions

The clean, irreversible, thermal transformation of acyl–isocyanide complexes into their isomeric iminoacyl–carbonyls has been documented for the first time, therefore demonstrating the greater thermodynamic stability of the latter compounds as compared to the former. While this conclusion applies strictly to the complexes described in this work, a survey of literature data suggests that it may be of general application and, therefore, that the formation of acyl derivatives in reactions in which the alkyl group can migrate to either a CO or CNR site may be kinetically driven. Irreversible isomerization of these known acyl–isocyanides seems feasible and may be accomplished in the near future.

Experimental Section

Microanalyses were carried out by the Analytical Service of the University of Sevilla. Infrared spectra were recorded as Nujol mulls or in an appropriate solvent on a Perkin–Elmer Model 684 spectrometer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were run on Varian XL-200 and Bruker AMX-300 and AMX-500 instruments. ^{31}P{^{1}H} NMR shifts were referenced to external 85% H_3PO_4, while ^{1}H and ^{13}C NMR shifts were referenced to the residual signals of the deuterated solvent employed, and all data are reported in ppm downfield from $SiMe_4$.

All preparation and manipulations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were dried and degassed before use. All reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was checked by elemental analysis, NMR techniques, and/or other suitable methods.

Preparation of Bp′Mo(η^2-C(O)R)(CO)(PMe$_3$)$_2$ Complexes (R = Me, 1a, 2a; CH$_2$SiMe$_3$, 1b, 2b; CH$_2$CMe$_3$, 1c, 2c). The preparation of all these compounds involves treating the appropriate Mo(η^2-C(O)R)Cl(CO)(PMe$_3$)$_3$[9b,f] precursors with the corresponding KBp′ reagents. The representative experimental procedure employed to synthesize BpMo(η^2-C(O)CH$_3$)(CO)(PMe$_3$)$_2$ (**1a**) was as follows.

The complex Mo(η^2-C(O)CH$_3$)Cl(CO)(PMe$_3$)$_3$ (0.43 g, 1 mmol) and KBp (0.23 g, 1.2 mmol) were stirred at room temperature in 50 mL of THF over a period of 2 h. The resulting mixture was then evaporated to dryness, and the residue was extracted with 40 mL of a 1:1 petroleum ether–Et$_2$O mixture. After the solution was centrifuged and cooled to −15 °C, compound **2a** was obtained as red crystals in 80% yield.

Starting with the appropriate chloro–acyl complexes and KBp or KBp*, we obtained compounds **1b**, **1c**, and **2a**–**2c** in similar yields by using analogous procedures. The Bp* derivatives are somewhat unstable in solution in the absence of free PMe$_3$ (note that 1 equiv of trimethylphosphine is released during the course of the above reaction) and break down disproportionately, upon stirring at room temperature, into a mixture of Bp*Mo(η^2-C(O)R)(CO)$_2$(PMe$_3$) and other unidentified products. For synthetic purposes, these Bp* derivatives may be generated in situ. Due to their very high solubility in common organic solvents, complexes **1b** and **2c** could not be isolated as pure solids.

BpMo(η^2-C(O)CH$_3$)(CO)(PMe$_3$)$_2$ (1a). Anal. Calcd for $C_{15}H_{29}N_4BO_2P_2Mo$: C, 38.7; H, 6.2; N, 12.0. Found: C, 39.2; H, 6.3; N, 11.4. IR (Nujol mull, cm^{-1}): 1789 (s), 1501 (m) (ν_{CO}). ^{1}H NMR (20 °C, C_6D_6): δ 0.94 (t, $J_{HP_{app}}$ = 3.5 Hz, 2 PMe$_3$), 2.36 (s, COCH$_3$), 5.93, 5.96 (t, $^3J_{HH}$ = 2.1 Hz, 2 CH), 7.20, 7.58, 7.58, 7.74 (d, $^3J_{HH}$ = 2.1 Hz, 4 CH). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 3.2 (s). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 14.1 (t, $J_{CP_{app}}$ = 10 Hz, 2 PMe$_3$), 27.1 (s, COCH$_3$), 103.8, 105.1, 135.6, 136.8, 137.4, 146.9 (s, 6 CH), 220.0 (t, $^2J_{CP}$ = 10 Hz, CO), 273.4 (dd, $^2J_{CP}$ = 20, 13 Hz, *C*OCH$_3$).

(19) (a) Cotton, J. D.; Crisp, G. T.; Latif, L. *Inorg. Chim. Acta* **1981**, *47*, 171. (b) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051. (c) Debad, J. D.; Legzdings, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 2094.

BpMo(η^2-C(O)CH$_2$SiMe$_3$)(CO)(PMe$_3$)$_2$ (1b). IR (THF solution, cm^{-1}): 1780 (s) (ν_{CO}). ^{1}H NMR (20 °C, C_6D_6): δ 0.19 (s, SiMe$_3$), 0.97 (t, $J_{HP_{app}}$ = 3.5 Hz, 2 PMe$_3$), 2.86 (s, COCH$_2$), 5.97, 5.98 (t, $^3J_{HH}$ = 2.1 Hz, 2 CH), 7.21, 7.56, 7.59, 7.74 (d, $^3J_{HH}$ = 2.1 Hz, 4 CH). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 2.4 (s). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ −0.3 (s, SiMe$_3$), 15.9 (t, $J_{CP_{app}}$ = 10 Hz, 2 PMe$_3$), 35.1 (s, *C*OCH$_2$), 103.6, 105.1, 135.6, 136.8, 137.9, 147.1 (s, 6 CH), 237.5 (t, $^2J_{CP}$ = 12 Hz, CO), 270.9 (t, $^2J_{CP}$ = 19 Hz, *C*OCH$_2$). ^{13}C-gated: δ 270.9 (tt, $^2J_{CP}$ = 19 Hz, $^2J_{CH}$ = 5 Hz).

BpMo(η^2-C(O)CH$_2$CMe$_3$)(CO)(PMe$_3$)$_2$ (1c). Anal. Calcd for $C_{19}H_{37}N_4BO_2P_2Mo$: C, 43.7; H, 7.1; N, 10.7. Found: C, 43.8; H, 7.7; N, 10.9. IR (Nujol mull, cm^{-1}): 1774 (s), 1509 (m) (ν_{CO}). ^{1}H NMR (20 °C, C_6D_6): δ 0.97 (t, $J_{HP_{app}}$ = 3.5 Hz, 2 PMe$_3$), 1.11 (s, CMe$_3$), 3.02 (s, COCH$_2$), 5.93, 5.97 (t, $^3J_{HH}$ = 2.1 Hz, 2 CH), 7.26, 7.58 (dd, $^3J_{HH}$ = 2.1, 0.4 Hz, 2 CH), 7.59, 7.71 (dd, $^3J_{HH}$ = 2.1, 1.0 Hz, 2 CH). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 1.8 (s). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 15.7 (t, $J_{CP_{app}}$ = 10 Hz, 2 PMe$_3$), 29.9 (s, C*Me*$_3$), 32.6 (s, *C*Me$_3$), 54.7 (s, CO*C*H$_2$), 103.7, 105.1, 135.6, 136.8, 137.7, 140.1 (s, 6 CH), 238.8 (t, $^2J_{CP}$ = 10 Hz, CO), 275.7 (t, $^2J_{CP}$ = 19 Hz, *C*OCH$_2$).

Bp*Mo(η^2-C(O)CH$_3$)(CO)(PMe$_3$)$_2$ (2a). Anal. Calcd for $C_{19}H_{37}N_4BO_2P_2Mo$: C, 43.7; H, 7.1; N, 10.7. Found: C, 42.4; H, 7.0; N, 10.0. IR (Nujol mull, cm^{-1}): 1780 (s), 1490 (m) (ν_{CO}). ^{1}H NMR (20 °C, $C_6D_5CD_3$): δ 1.18 (t, $J_{HP_{app}}$ = 2.9 Hz, 2 PMe$_3$), 2.05, 2.48, 2.52, 2.60 (s, 4 CMe), 2.74 (s, COCH$_3$), 5.77, 5.88 (s, 2 CH). ^{31}P{^{1}H} NMR (20 °C, $C_6D_5CD_3$): δ 3.3 (br s). ^{31}P{^{1}H} NMR (−50 °C, THF/CD_3COCD_3): δ −0.3, 4.3 (AB spin system, $^2J_{P_AP_B}$ = 143 Hz).

Bp*Mo(η^2-C(O)CH$_2$SiMe$_3$)(CO)(PMe$_3$)$_2$ (2b). Anal. Calcd for $C_{22}H_{45}N_4BO_2SiP_2Mo$: C, 44.4; H, 7.6; N, 9.4. Found: C, 44.2; H, 7.8; N, 9.2. IR (Nujol mull, cm^{-1}): 1779 (s), 1480 (m) (ν_{CO}). ^{1}H NMR (20 °C, C_6D_6): δ 0.28 (s, SiMe$_3$), 1.08 (br s, 2 PMe$_3$), 1.99, 2.46 (s, 2 CMe), 2.31 (br s, 2 CMe), 3.11 (vbr s, COCH$_2$), 5.65, 5.72 (s, 2 CH). ^{1}H NMR (−50 °C, $C_6D_5CD_3$): δ 0.18 (s, SiMe$_3$), 0.66 (d, $^2J_{HP}$ = 5.7 Hz, PMe$_3$), 1.13 (d, $^2J_{HP}$ = 6.8 Hz, PMe$_3$), 1.87, 2.19, 2.25, 2.36 (s, 4 CMe), 2.52, 3.52 (AB spin system, $^2J_{H_AH_B}$ = 10.5 Hz, COCH$_A$H$_B$), 5.49, 5.53 (s, 2 CH). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 3.2 (br s). ^{31}P{^{1}H} NMR (−50 °C, $C_6D_5CD_3$): δ −0.3, 4.3 (AB spin system, $^2J_{P_AP_B}$ = 140 Hz). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 13.8, 14.0, 15.1, 17.9 (s, 4 C*Me*), 16.2 (br s, 2 PMe$_3$), 37.4 (s, CO*C*H$_2$), 106.6, 107.8, (s, 2 CH), 144.9, 145.9, 151.8, 154.4 (s, 4 *C*Me), 238.4 (t, $^2J_{CP}$ = 13 Hz, CO), 267.0 (t, $^2J_{CP}$ = 19 Hz, *C*OCH$_2$).

Bp*Mo(η^2-C(O)CH$_2$CMe$_3$)(CO)(PMe$_3$)$_2$ (2c). IR (THF solution, cm^{-1}): 1790 (s) (ν_{CO}). ^{1}H NMR (20 °C, C_6D_6): δ 1.03 (br s, 2 PMe$_3$), 1.20 (s, CMe$_3$), 1.90, 2.28, 2.31, 2.41 (s, 4 CMe), 3.40 (vbr s, COCH$_2$), 5.60, 5.71 (s, 2 CH). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 1.1 (s). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 13.6, 13.9, 14.9, 17.6 (s, 4 C*Me*), 16.2 (br s, 2 PMe$_3$), 30.0 (s, C*Me*$_3$), 32.4 (s, *C*Me$_3$), 56.8 (s, CO*C*H$_2$), 106.7, 107.9 (s, 2 CH), 144.6, 145.8, 151.4, 153.8 (s, 4 *C*Me), 236.6 (br s, CO), 267.6 (br s, *C*OCH$_2$).

Preparation of Bp′Mo(η^2-C(O)R)(CN-*t*-Bu)(CO)(PMe$_3$) (R = Me, 4a; CH$_2$SiMe$_3$, 4b; CH$_2$CMe$_3$, 3c, 4c). Neat CN-*t*-Bu (0.12 mL, ca. 1 mmol) was added to a stirred solution of **2a** (prepared in situ in 1 mmol scale reaction) in THF (60 mL) at −10 °C. The initially red solution immediately became orange and was stirred for 5 min at −10 °C. This temperature was kept during the workup procedure. The solvent was then evaporated in vacuo, and the remaining residue was crystallized from 1:1 petroleum ether–Et$_2$O mixture at −15 °C to obtain Bp*Mo(η^2-C(O)CH$_3$)(CO)(CN-*t*-Bu)(PMe$_3$) (**4a**) as yellow-orange crystals in 75% yield.

Using the appropriate starting materials, we obtained related Bp′Mo(η^2-C(O)R)(CO)(CN-*t*-Bu)(PMe$_3$) complexes **3c**, **4b**, and **4c** by the above procedure in similar yields as red-orange crystals. They are more stable than **4a** and can be handled in solution at room temperature.

BpMo(η^2-C(O)CH$_2$CMe$_3$)(CN-*t*-Bu)(CO)(PMe$_3$) (3c). Anal. Calcd for $C_{21}H_{37}N_5BO_2PMo$: C, 47.6; H, 7.0; N, 13.2. Found: C, 47.9; H, 7.1; N, 12.6. IR (Nujol mull, cm^{-1}): 2091 (s) (ν_{CN}), 1797 (s), 1571 (m) (ν_{CO}). ^{1}H NMR (20 °C, C_6D_6): δ 1.03 (s, C*Me*$_3$), 1.18 (s, NC*Me*$_3$), 1.23 (d, J_{HP} = 8.7 Hz, PMe$_3$), 3.35, 3.59 (AB spin system, $^2J(H_AH_B)$ = 16.4 Hz, COCH$_A$H$_B$), 5.99, 6.04 (t, $^3J_{HH}$ = 2.1 Hz, 2 CH), 7.23, 7.58 (dd, $^3J_{HH}$ = 2.1, 0.7 Hz, 2 CH), 7.65, 8.04 (dd, $^3J_{HH}$ = 2.1, 0.6 Hz, 2 CH). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 9.7 (s). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 16.8 (d, $^2J_{CP}$ = 26 Hz, PMe$_3$), 29.6 (s, C*Me*$_3$), 30.6 (s, NC*Me*$_3$), 32.1 (s, *C*Me$_3$), 56.3 (s, N*C*Me$_3$), 58.2 (s, CO*C*H$_2$), 104.0,

104.9, 135.5, 136.3, 141.5, 144.9 (s, 6 *C*H), 182.4 (d, $^2J_{CP}$ = 25 Hz, *C*NCMe$_3$), 233.4 (d, $^2J_{CP}$ = 15 Hz, CO), 269.4 (d, $^2J_{CP}$ = 13 Hz, *C*OCH$_2$).

Bp*Mo(η^2-C(O)CH$_3$)(CN-*t*-Bu)(CO)(PMe$_3$) (4a). Anal. Calcd for $C_{21}H_{37}N_5BO_2PMo$: C, 47.6; H, 7.0; N, 13.2. Found: C, 47.7; H, 7.1; N, 13.2. IR Nujol mull, cm^{-1}): 2091 (s) (ν_{CN}), 1805 (s), 1570 (m) (ν_{CO}). ^{1}H NMR (−8 °C, $C_6D_5CD_3$): δ 0.94 (s, NC*Me$_3$*), 1.35 (d, J_{HP} = 8.7 Hz, PMe$_3$), 2.17, 2.28, 2.33, 2.58 (s, 4 CMe), 2.94 (s, COCH$_3$), 5.63, 5.70 (s, 2 CH). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 15.6 (s). ^{13}C{^{1}H} NMR (−30 °C, CD_3COCD_3): δ 13.1 (s, 2 C*Me*), 14.4, 14.8 (s, 2 C*Me*), 17.3 (d, $^2J_{CP}$ = 29 Hz, PMe$_3$), 31.0 (s, NC*Me$_3$*), 31.6 (s, CO*C*H$_3$), 58.0 (s, N*C*Me$_3$), 106.4, 106.6 (s, 2 CH), 143.1, 143.6, 149.5, 151.3 (s, 4 *C*Me), 174.2 (d, $^2J_{CP}$ = 29 Hz, *C*NCMe$_3$), 232.3 (d, $^2J_{CP}$ = 20 Hz, CO), 272.8 (d, $^2J_{CP}$ = 14 Hz, *C*OCH$_2$).

Bp*Mo(η^2-C(O)CH$_2$SiMe$_3$)(CN-*t*-Bu)(CO)(PMe$_3$) (4b). Anal. Calcd for $C_{24}H_{45}N_5BO_2SiPMo$: C, 47.2; H, 7.5; N, 11.6. Found: C, 47.9; H, 8.1; N, 11.0. IR (Nujol mull, cm^{-1}): 2048 (s) (ν_{CN}), 1793 (s), 1550 (m) (ν_{CO}). ^{1}H NMR (20 °C, CD_3COCD_3): δ 0.25 (s, SiMe$_3$), 1.44 (d, J_{HP} = 8.6 Hz, PMe$_3$), 1.62 (s, NCMe$_3$), 2.01, 2.15, 2.26, 2.27 (s, 4 CMe), 3.05, 3.90 (AB spin system, $^2J(H_AH_B)$ = 11.2 Hz, COCH$_A$H$_B$), 5.59, 5.83 (s, 2 CH). ^{31}P{^{1}H} NMR (20 °C, CD_3COCD_3): δ 17.8 (s). ^{13}C{^{1}H} NMR (20 °C, CD_3COCD_3): δ 0.2 (s, SiMe$_3$), 13.1 (s, 2 C*Me*), 14.8, 15.2 (s, 2 C*Me*), 17.5 (d, $^2J_{CP}$ = 28 Hz, PMe$_3$), 31.2 (s, NC*Me$_3$*), 39.1 (s, CO*C*H$_2$), 57.9 (s, N*C*Me$_3$), 106.1, 106.6 (s, 2 CH), 143.0, 143.7, 149.5, 151.5 (s, 4 *C*Me), 178.2 (d, $^2J_{CP}$ = 28 Hz, *C*NCMe$_3$), 235.1 (d, $^2J_{CP}$ = 17 Hz, CO), 269.7 (d, $^2J_{CP}$ = 14 Hz, *C*OCH$_2$).

Bp*Mo(η^2-C(O)CH$_2$CMe$_3$)(CN-*t*-Bu)(CO)(PMe$_3$) (4c). Anal. Calcd for $C_{25}H_{45}N_5BO_2PMo$: C, 51.3; H, 7.7; N, 12.0. Found: C, 51.5; H, 8.1; N, 12.0. IR (Nujol mull, cm^{-1}): 2033 (s) (ν_{CN}), 1807 (s), 1565 (m) (ν_{CO}). ^{1}H NMR (20 °C, C_6D_6): δ 1.01 (s, C*Me$_3$*), 1.27 (s, NC*Me$_3$*), 1.39 (d, J_{HP} = 8.5 Hz, PMe$_3$), 2.21, 2.29, 2.35, 2.58 (s, 4 CMe), 3.33, 3.92 (AB spin system, $^2J(H_AH_B)$ = 17.7 Hz, COCH$_A$H$_B$), 5.66, 5.73 (s, 2 CH). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 14.3 (s). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 12.9 (s, 2 C*Me*), 14.3, 14.8 (s, 2 C*Me*), 17.3 (d, $^2J_{CP}$ = 26 Hz, PMe$_3$), 29.5 (s, C*Me$_3$*), 30.5 (s, NC*Me$_3$*), 31.7 (s, *C*Me$_3$), 56.0 (s, N*C*Me$_3$), 60.0 (s, CO*C*H$_2$), 105.8, 106.3 (s, 2 CH), 142.8, 143.1, 148.5, 150.9 (s, 4 *C*Me), 180.9 (d, $^2J_{CP}$ = 28 Hz, *C*NCMe$_3$), 233.2 (d, $^2J_{CP}$ = 20 Hz, CO), 269.6 (d, $^2J_{CP}$ = 13 Hz, *C*OCH$_2$).

Preparation of Bp'Mo(η^2-C(N-*t*-Bu)R)(CO)$_2$(PMe$_3$) (R = Me, 5a, 6a; CH$_2$SiMe$_3$, 6b; CH$_2$CMe$_3$, 5c). A red solution of complex **2a** (1 mmol) in THF was treated with CN-*t*-Bu (0.12 mL, ca. 1 mmol) at ambient temperature. After 3 h of stirring, the solvent was evaporated under reduced pressure, and the residue was extracted with a 1:1 petroleum ether−Et$_2$O mixture. Further centrifugation and cooling at −15 °C overnight produced red crystals of Bp'Mo(η^2-C(N-*t*-Bu)CH$_3$)-(CO)$_2$(PMe$_3$) (**6a**) in 80% isolated yield.

Starting from acyls **1** and **2**, we obtained the remaining complexes by a procedure analogous to that described for **6a**. Longer reaction times are required for the formation of **5c** (3 days) and **6b** (7 days) at room temperature, but at higher temperatures (50−70 °C), the reactions are considerably faster.

Alternatively, iminoacyl−carbonyls **5** and **6** can be prepared in essentially quantitative yields by thermal isomerization (10−70 °C) of the corresponding acyl−isocyanide derivatives. It should be mentioned, however, that complex **4c** fails to isomerize to the expected iminoacyl (less than 10% conversion) when its solutions are heated at 70 °C. Under these conditions, a competitive transformation, which results in the hydroboration of the acyl ligand, takes place.[15]

BpMo(η^2-C(N-*t*-Bu)CH$_3$)(CO)$_2$(PMe$_3$) (5a). Anal. Calcd for $C_{17}H_{31}N_5BO_2PMo$: C, 43.0; H, 6.6; N, 14.7. Found: C, 42.9; H, 6.2; N, 14.8. IR (Nujol mull, cm^{-1}): 1914 (s), 1807 (s) (ν_{CO}), 1748 (m) (ν_{CN}). ^{1}H NMR (20 °C, C_6D_6): δ 0.57 (s, NC*Me$_3$*), 1.12 (d, J_{HP} = 8.5 Hz, PMe$_3$), 2.51 (s, C(NCMe$_3$)C*H$_3$*), 5.96 (t, $^3J_{HH}$ = 2.1 Hz, 2 CH), 7.43, 7.62 (d, $^3J_{HH}$ = 2.1 Hz, 4 CH). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 5.1 (s). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 17.1 (d, $^2J_{CP}$ = 25 Hz, PMe$_3$), 20.1 (s, C(NCMe$_3$)*C*H$_3$), 28.5 (s, NC*Me$_3$*), 57.7 (s, N*C*Me$_3$), 104.5, 136.1, 143.9 (s, 6 *C*H), 189.8 (d, $^2J_{CP}$ = 10 Hz, *C*NCMe$_3$), 236.4 (d, $^2J_{CP}$ = 18 Hz, 2 CO).

BpMo(η^2-C(N-*t*-Bu)CH$_2$CMe$_3$)(CO)$_2$(PMe$_3$) (5c). Anal. Calcd for $C_{21}H_{37}N_5BO_2PMo$: C, 47.6; H, 7.0; N, 13.2. Found: C, 47.4; H, 7.4; N, 13.1. IR (Nujol mull, cm^{-1}): 1914 (s), 1810 (s) (ν_{CO}), 1716 (m) (ν_{CN}). ^{1}H NMR (20 °C, C_6D_6): δ 0.56 (s, CMe$_3$), 1.17 (d, J_{HP} = 8.6 Hz, PMe$_3$), 1.23 (s, NC*Me$_3$*), 3.19 (s, C(NCMe$_3$)CH$_2$), 6.00 (t, $^3J_{HH}$ = 2.1 Hz, 2 CH), 7.48, 7.63 (d, $^3J_{HH}$ = 2.1 Hz, 4 CH). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 5.1 (s). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 17.2 (d, $^2J_{CP}$ = 26 Hz, PMe$_3$), 28.8 (s, C*Me$_3$*), 30.4 (s, NC*Me$_3$*), 32.9 (s, *C*Me$_3$), 45.3 (s, C(NCMe$_3$)*C*H$_2$), 58.7 (s, N*C*Me$_3$), 104.6, 136.1, 143.7 (s, 6 *C*H), 190.7 (d, $^2J_{CP}$ = 11 Hz, *C*NCMe$_3$), 240.7 (d, $^2J_{CP}$ = 19 Hz, 2 CO).

Bp*Mo(η^2-C(N-*t*-Bu)CH$_3$)(CO)$_2$(PMe$_3$) (6a). Anal. Calcd for $C_{21}H_{37}N_5BO_2PMo$: C, 47.6; H, 7.0; N, 13.2. Found: C, 47.6; H, 7.1; N, 13.1. IR (Nujol mull, cm^{-1}): 1905 (s), 1795 (s) (ν_{CO}), 1752 (m) (ν_{CN}). ^{1}H NMR (20 °C, C_6D_6): δ 0.62 (s, NC*Me$_3$*), 1.35 (d, J_{HP} = 8.6 Hz, PMe$_3$), 2.74 (s, C(NCMe$_3$)C*H$_3$*), 2.30, 2.33 (s, 4 CCH$_3$), 5.71 (s, 2 CH). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 9.0 (s). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 13.2, 16.2 (s, 4 C*Me*), 17.7 (d, $^2J_{CP}$ = 28 Hz, PMe$_3$), 21.7 (s, C(NCMe$_3$)*C*H$_3$), 29.1 (s, NC*Me$_3$*), 57.0 (s, N*C*Me$_3$), 106.7 (s, 2 *C*H), 144.1, 150.7 (s, 4 *C*CH$_3$), 192.4 (d, $^2J_{CP}$ = 10 Hz, *C*NCMe$_3$), 235.7 (d, $^2J_{CP}$ = 19 Hz, 2 CO).

Bp*Mo(η^2-C(N-*t*-Bu)CH$_2$SiMe$_3$)(CO)$_2$(PMe$_3$) (6b). Anal. Calcd for $C_{24}H_{45}N_5BO_2SiPMo$: C, 47.9; H, 7.5; N, 11.6. Found: C, 47.6; H, 7.3; N, 11.4. IR (Nujol mull, cm^{-1}): 1918 (s), 1801 (s) (ν_{CO}), 1700 (m) (ν_{CN}). ^{1}H NMR (20 °C, C_6D_6): δ 0.31 (s, SiMe$_3$), 0.71 (s, NC*Me$_3$*), 1.36 (d, J_{HP} = 8.5 Hz, PMe$_3$), 2.35, 2.39 (s, 4 CCH$_3$), 3.23 (s, C(NCMe$_3$)C*H$_2$*), 5.74 (s, 2 CH). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 8.1 (s). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 0.4 (s, SiMe$_3$), 13.3, 16.3 (s, 4 C*Me*), 17.2 (d, $^2J_{CP}$ = 27 Hz, PMe$_3$), 28.9 (s, C(N-*t*-Bu)*C*H$_2$), 29.1 (s, NC*Me$_3$*), 56.6 (s, N*C*Me$_3$), 106.4 (s, 2 *C*H), 143.9, 150.4 (s, 4 *C*CH$_3$), 190.8 (d, $^2J_{CP}$ = 10 Hz, *C*NCMe$_3$), 239.1 (d, $^2J_{CP}$ = 21 Hz, 2 CO).

Bp*Mo(η^2-C(N-*t*-Bu)CH$_2$CMe$_3$)(CO)$_2$(PMe$_3$) (6c). ^{1}H NMR (20 °C, C_6D_6): δ 1.06 (s, NC*Me$_3$*), 1.26 (s, CMe$_3$), 1.37 (d, J_{HP} = 8.6 Hz, PMe$_3$), 2.33, 2.37 (s, 4 CCH$_3$), 3.40 (s, C(NCMe$_3$)C*H$_2$*), 5.73 (s, 2 CH). ^{31}P{^{1}H} NMR (20 °C, C_6D_6): δ 7.7 (s). ^{13}C{^{1}H} NMR (20 °C, C_6D_6): δ 13.3, 16.3 (s, 4 C*Me*), 17.1 (d, $^2J_{CP}$ = 28 Hz, PMe$_3$), 29.1 (s, C*Me$_3$*), 30.3 (s, NC*Me$_3$*), 32.8 (s, *C*Me$_3$), 47.2 (s, C(N-*t*-Bu)*C*H$_2$), 57.0 (s, N*C*Me$_3$), 106.4 (s, 2 *C*H), 143.9, 150.1 (s, 4 *C*CH$_3$), 193.7 (d, $^2J_{CP}$ = 10 Hz, *C*NCMe$_3$), 241.1 (d, $^2J_{CP}$ = 21 Hz, 2 CO).

Kinetic Studies of the Isomerization of η^2-Acyl 3c into η^2-Iminoacyl 5c. The disappearance of **3c** was monitored by ^{31}P{^{1}H} NMR spectroscopy for a period of about 4 half-lives. The reaction is well-behaved and produces **5c** as the only detectable product. The rate of the reaction was measured at four different temperatures (315, 323, 331, and 339 K); duplicate experiments being performed in each case. The experimental procedure was as follows. On a vacuum line, a solution of **3c** in toluene (around 0.08 M) was transferred under N$_2$ into a 5 mm NMR tube, and it was frozen and degassed. The tube was then flame sealed and placed in a constant temperature bath (the uncertainty in the temperature was ±0.1 °C) from which it was removed at appropriate time intervals and cooled in iced water to quench the reaction. In order to avoid the possible interference on the kinetic measurements of an internal reference, a solution of PPh$_3$ in acetone-d_6 (around 0.04 M) was employed as an external standard. This reference was placed in a 10 mm NMR tube surrounding the sealed 5 mm NMR tube that contained the toluene solution used for the kinetic studies. Its ^{31}P{^{1}H} NMR spectrum was then recorded at 20 °C using a 10 mm probe on a Varian XL-200 spectrometer. In each experiment, the acquisition was performed using a pulse delay of 5 times the expected relaxation time of the ^{31}P nucleus and completed rapidly as compared to the time of reaction at 20 °C.

X-ray Structure Determinations of 4b and 6b. A summary of the fundamental crystal data is given in Table 1. Crystals of **4b** and **6b** were coated with an epoxy resin and mounted in a kappa diffractometer. The cell dimensions were refined by least-squares fitting of 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, P, and Si were taken from ref 20. The structures were solved by Patterson and Fourier methods. An empirical absorption correction was applied at the end of the isotropic refinement.[21]

Compound **4b** crystallizes in the $P2_1/c$ space group, and **6b** crystallizes in the $C2/c$ space group. In order to prevent bias on ΔF

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vs F_0 or (sin θ/λ), in the structure determination of **4b**, weights were assigned as $w = 1/(a+b|F_o|)^2$, with the following coefficients: $|F_0| < 27$, $a = 6.12$, $b = -0.13$; $|F_0| > 27$, $a = 0.96$, $b = 0.02$.[22] A final refinement was undertaken with fixed isotropic factors and coordinates for all H atoms. Final difference synthesis showed no significant electron density. Final values were $R = 0.062$ and $R_w = 0.064$ for **4b** and $R = 0.032$ and $R_w = 0.036$ for **6b**. Most of the calculations were carried out with the X-ray 80 System.[23]

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Supplementary Material Available: Crystallographic tables for **4b** and **6b** including positional and thermal parameters, fractional coordinates, and selected bond lengths and angles (9 pages); tables of observed and calculated structure factors (90 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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