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Reactivity studies of η^2-acyl complexes of molybdenum. Kinetics of η^2-acyl to η^2-iminoacyl isomerization in their reactions with isocyanides

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Treatment of the dihaptoacyls $[Mo\{\eta^2\text{-}C(O)R\}L(CO)(PMe_3)_2]$ with carbon monoxide afforded the dicarbonyl derivatives $[Mo\{\eta^2\text{-}C(O)R\}L(CO)_2(PMe_3)]$ [L = $H_2B(pz)_2$ or $H_2B(dmpz)_2$; pz = pyrazolyl, dmpz = 3,5-dimethylpyrazolyl; R = Me, CH_2SiMe_3 or CH_2CMe_3]. The analogous reactions with isocyanides, CNR', yielded two types of products, namely the acyl-isocyanides $[Mo\{\eta^2\text{-}C(O)R\}L(CO)(CNR')(PMe_3)]$ or the η^2-iminoacyls $[Mo\{\eta^2\text{-}C(NR')R\}L(CO)_2(PMe_3)]$ (R' = CNC_6H_3Me-2,6, CNC_6H_4OMe-*p*, $CNCH_2Ph$ or CNC_6H_{11}) depending upon the nature of the bis(pyrazolyl)borate ligand and the R group. Kinetic studies of the transformation $[Mo\{\eta^2\text{-}C(O)CH_2SiMe_3\}\{H_2B(dmpz)_2\}CO(CNR')(PMe_3)] \longrightarrow [Mo\{\eta^2\text{-}C(NR')CH_2SiMe_3\}\{H_2B(dmpz)_2\}(CO)_2(PMe_3)]$ (R' = 2,6-$Me_2C_6H_3$) show first-order behaviour and are consistent with a mechanism involving deinsertion of CO to give a seven-co-ordinate alkyl intermediate in the rate-determining step.

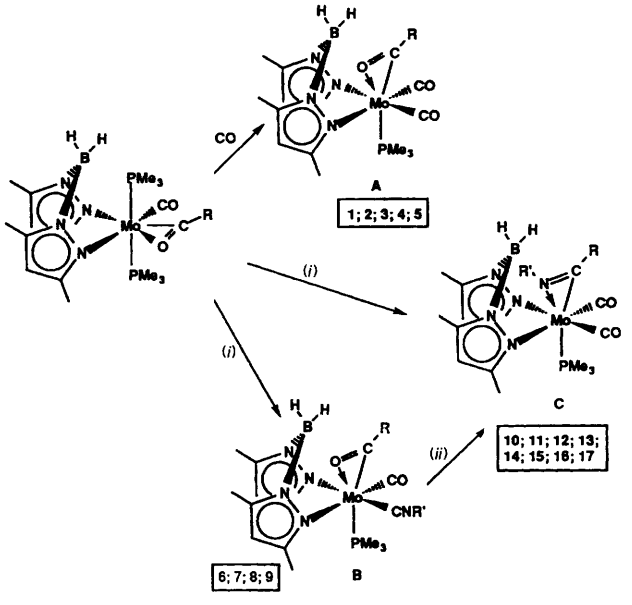
Transition-metal acyl complexes play an important role in a number of organometallic reactions.[1] Bidentate co-ordination is usually the preferred binding mode of the acyl group in complexes of the early transition metals,[1,2] including the 6d metals.[3,4] Strong M–η^2-C(O)R linkages are very often encountered and consequently many reactions of these compounds with Lewis bases proceed with substitution of other ligands without altering the co-ordination mode of the acyl moiety.

Recent work from our laboratory has shown that the interaction of the η^2-acyls $[Mo\{\eta^2\text{-}C(O)R\}L(CO)(PMe_3)_2]$ [L = unsubstituted and 3,5-dimethyl-substituted dihydrobis(pyrazolyl)borate, $H_2B(pz)_2$ and $H_2B(dmpz)_2$] with CNBu^t proceeds initially with PMe_3 displacement by the isocyanide, followed by isomerization to the thermodynamically more stable η^2-iminoacyl-carbonyls $[Mo\{\eta^2\text{-}C(NBu^t)R\}L(CO)_2(PMe_3)]$.[5] Since this report constitutes only the first well documented example of an isomerization of this type, we have sought its generalization by the use of other isocyanides with different electronic and steric properties and therefore migrating capability.[6] Here we discuss the results of this study, together with the outcome of the substitution reactions of the above and other related η^2-acyls of Mo with CO.

Results and Discussion

The new compounds described contain a bidentate bis(pyrazolyl)borate ligand[7] and are of the types **A**–**C**. Scheme 1 shows the synthetic procedure employed and includes also the combinations of the co-ligands which have been utilized.

While acyls of composition $[Mo\{\eta^2\text{-}C(O)R\}L(CO)(PMe_3)_2]$ (for every combination of L with R = Me, CH_2SiMe_3 or CH_2CMe_3) interact with CO to afford the corresponding dicarbonyl products **A** (Scheme 1), the analogous reaction with isocyanides, CNR', may give compounds with structure **B** or **C**. For example, in the $H_2B(pz)_2$ system all the reactions investigated, which comprise those of $[Mo\{\eta^2\text{-}C(O)Me\}\{H_2B(pz)_2\}(CO)(PMe_3)_2]$ with CNR' (R' = $C_6H_3Me_2$-2,6 or C_6H_4OMe-*p*) plus those of the neopentyl-derived η^2-acyl with CNR' (R' = CH_2Ph, C_6H_{11} or $C_6H_3Me_2$-2,6), provide the η^2-iminoacyl (structure **C**) even when they are performed at low temperatures (*ca.* −10 °C). Hence, it seems clear that, for these conversions, the initial substitution of PMe_3 by CNR' is followed by fast acyl-to-iminoacyl rearrangement to the observed η^2-iminoacyl products. These results are in agreement with those found in the interaction of the molybdenum η^2-acyls with CNBu^t although for the latter systems the bulkiness of the isocyanide fragment allows the isolation of stable η^2-acyl-isocyanide compounds of type **B**.[5]



	L	R	CO/CNR'
1	$H_2B(pz)_2$	Me	CO
2	$H_2B(pz)_2$	CH_2CMe_3	CO
3	$H_2B(dmpz)_2$	Me	CO
4	$H_2B(dmpz)_2$	CH_2SiMe_3	CO
5	$H_2B(dmpz)_2$	CH_2CMe_3	CO
6	$H_2B(dmpz)_2$	CH_2SiMe_3	$CNC_6H_3Me_2$-2,6
7	$H_2B(dmpz)_2$	CH_2CMe_3	$CNCH_2Ph$
8	$H_2B(dmpz)_2$	CH_2CMe_3	CNC_6H_{11}
9	$H_2B(dmpz)_2$	CH_2CMe_3	$CNC_6H_3Me_2$-2,6
10	$H_2B(pz)_2$	Me	$CNC_6H_3Me_2$-2,6
11	$H_2B(pz)_2$	Me	CNC_6H_4OMe-*p*
12	$H_2B(pz)_2$	CH_2CMe_3	$CNCH_2Ph$
13	$H_2B(pz)_2$	CH_2CMe_3	CNC_6H_{11}
14	$H_2B(pz)_2$	CH_2CMe_3	$CNC_6H_3Me_2$-2,6
15	$H_2B(dmpz)_2$	Me	$CNC_6H_3Me_2$-2,6
16	$H_2B(dmpz)_2$	Me	CNC_6H_4OMe-*p*
17	$H_2B(dmpz)_2$	CH_2SiMe_3	$CNC_6H_3Me_2$-2,6

Scheme 1 (*i*) CNR'; (*ii*) heat

In turn, for the $H_2B(dmpz)_2$ system the interaction of $[Mo\{\eta^2\text{-}C(O)Me\}\{H_2B(dmpz)_2\}(CO)(PMe_3)_2]$ with CNR (R' = $C_6H_3Me_2$-2,6 or C_6H_4OMe-*p*) also furnishes directly η^2-iminoacyls of structure **C** whilst treatment of $[Mo\{\eta^2\text{-}C(O)CH_2SiMe_3\}\{H_2B(dmpz)_2\}(CO)(PMe_3)_2]$ with $CNC_6H_3Me_2$-2,6 and of $[Mo\{\eta^2\text{-}C(O)CH_2CMe_3\}\{H_2B(dmpz)_2\}(CO)(PMe_3)_2]$ with CNR' (R = CH_2Ph, C_6H_{11} or $C_6H_3Me_2$-2,6) allows the isolation of the expected η^2-acyls with structure **B**. Hence, the facility with which the transformation of the acyls $Mo\{\eta^2\text{-}C(O)R\}(CNR')$ into the iminoacyls $Mo\{\eta^2\text{-}C(NR')R\}(CO)$ takes place varies in the order $H_2B(pz)_2$ > $H_2B(dmpz)_2$ and Me > CH_2SiMe_3 > CH_2CMe_3. Iminoacyl formation is therefore favoured for the least sterically demanding combination of the L and R fragments. Finally, in this regard, it should be mentioned that complex **6** converts slowly at room temperature into **17**, while the η^2-acyls derived from the bulkier neopentyl group, **7**–**9**, are stable at room temperature with respect to their transformation into the corresponding η^2-iminoacyls. This rearrangement occurs however, at higher temperatures (*ca.* 60 °C) but it is still so slow that a competitive reaction leading to hydroboration of the η^2-acyl fragment occurs preferentially.[8]

All the transformations represented in Scheme 1 give high yields of the corresponding products which are usually isolated by crystallization from Et_2O or light-petroleum (b.p. 40–60 °C)–Et_2O mixtures, in the form of red-orange or yellow crystalline solids. They can be readily characterized by spectroscopy (see Experimental section). The IR spectra of the acyls $[Mo\{\eta^2\text{-}C(O)R\}L(L')(CO)PMe_3]$ (L' = PMe_3, starting material; CO, structure **A**; CNR', **B**) display $\nu(CO)_{acyl}$ in the expected region[1] of 1625–1450 cm^{-1}. Within this range the stretching frequency shifts to lower wavenumbers as the electron-donor properties of L' increase: L' = CO, 1600–1560; CNR', 1580–1550; PMe_3, 1500–1480 cm^{-1}. This clearly reflects an increase in the same direction of the back donation from the metal centre to the acyl ligand. A parallel decrease is observed in the value of ν(CO) for the terminal carbonyl (*ca.* 1940 and 1850, L = CO; 1800, CNR'; 1775 cm^{-1}, PMe_3). The η^2-iminoacyls (structure **C**) are characterized by two strong terminal carbonyl stretchings in the vicinity of 1925 and 1800 cm^{-1} as well as by a medium-intensity absorption at *ca.* 1700 cm^{-1} due to the iminoacyl ligand. This supports the dihapto binding mode proposed for this functionality.[1,9] Since compounds with structures **A** and **C** have the same stereochemistry and differ only in the nature of the Mo–η^2-C(X)R linkage, a comparison of the donor properties of these two functionalities can be attempted. The already noted values of ν(CO) (1940, 1850 for the η^2-acyls; 1925, 1800 cm^{-1}, η^2-iminoacyls) indicate an overall higher donor ability of the η^2-iminoacyl entities as compared to the analogous η^2-acyl groups.

Best support for the structures assigned to the above complexes comes from NMR studies. Thus the η^2-acyls display the $^{13}C\text{-}\{^1H\}$ resonance of the acyl carbon in the region δ 275–250, while for the η^2-iminoacyls the Mo–$^{13}C(NR')R$ signal appears at δ 210–190. The above values are well in the range characteristic of compounds of this type. For the dicarbonyl complexes (**A** and **C**) the two carbonyls and the two pyrazolyl rings of the L ligand are equivalent at room temperature. As for other η^2-acyl complexes, this is probably due to a relatively low-energy fluxional process which creates an effective plane of symmetry.[10]

As already mentioned, of the isolated compounds with structure type **B** the $H_2B(dmpz)_2$–CH_2SiMe_3 derivative **6** is thermally stable at room temperature for moderate intervals of time, although it is converted into the η^2-iminoacyl isomer **17** over a period of several hours ($t_{\frac{1}{2}}$ = 0.75 h). In order to gain mechanistic information on this isomerization reaction, in particular with respect to the influence of the isocyanide ligand on the reaction rate, kinetic studies have been undertaken. Two closely related η^2-acyl-isocyanide derivatives were chosen:

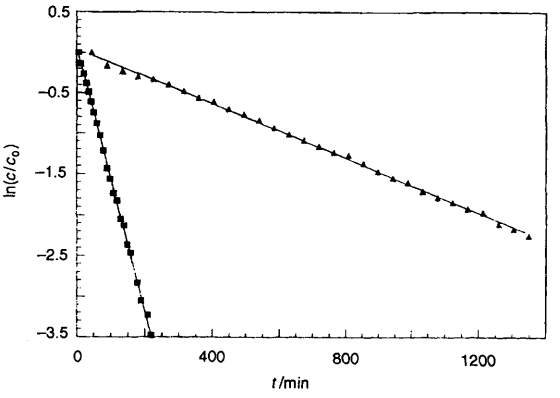


Fig. 1 First-order kinetic plots for the transformation of complex **6** (■) and $[Mo\{\eta^2\text{-}C(O)CH_2SiMe_3\}\{H_2B(dmpz)_2\}(CO)(CNBu^t)(PMe_3)]$ (▲) into the corresponding iminoacyl complexes

complex **6** and the already reported $[Mo\{\eta^2\text{-}C(O)CH_2SiMe_3\}\{H_2B(pz)_2\}(CO)(CNBu^t)(PMe_3)]$.[5] As can be seen, they contain identical sets of co-ligands with the only exception of the isocyanide groups, CNR' (R = $C_6H_3Me_2$-2,6 or Bu^t), their choice being influenced by their very different insertion aptitudes. The greater propensity of the aromatic isocyanide, $CNC_6H_3Me_2$-2,6, to undergo insertion reactions, as compared with the aliphatic $CNBu^t$, is well documented.[6,11]

The rates of the two reactions can be conveniently measured at room temperature by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. Both transformations follow first-order kinetics, the analysis of the data (Fig. 1) recorded over a period of *ca.* four half-lives yielding rate constants of 1.84×10^{-3} and 1.60×10^{-2} s^{-1} for the $CNBu^t$ and $CNC_6H_3Me_2$-2,6 derivatives. As expected, $CNC_6H_3Me_2$-2,6 inserts faster than $CNBu^t$, but the difference of only one order of magnitude in the k_{obs} values seems in agreement with a rate-determining step involving deinsertion of CO from the original η^2-acyl to generate a sterically congested seven-co-ordinate alkyl intermediate, followed by fast isocyanide insertion. This mechanistic hypothesis also finds support in the already cited influence of the steric effects of the L and R fragments on the reaction rate.

Experimental

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

All preparations and manipulations were carried out under oxygen-free nitrogen or argon, following conventional Schlenk techniques. Solvents were dried and degassed before use.

All reagents were either obtained from commercial suppliers or prepared according to published procedures. The complex $[Mo\{\eta^2\text{-}C(O)CH_2SiMe_3\}\{H_2B(dmpz)_2\}(CO)(CNBu^t)(PMe_3)]$ used for the kinetic studies was prepared as reported previously.[5] Analytical and spectroscopic data for the new complexes are given in Tables 1 and 2.

Preparations

$[Mo\{\eta^2\text{-}C(O)R\}L(CO)_2(PMe_3)]$, (structure A). Through a solution of $[Mo\{\eta^2\text{-}C(O)Me\}\{H_2B(pz)_2\}(CO)(PMe_3)_2]$[5] (0.46 g, 0.5 mmol) in tetrahydrofuran (thf) (50 cm^3), carbon monoxide was slowly bubbled at room temperature until the

Table 1 Analytical, IR and ^1H NMR data for the compounds $[Mo\{\eta^2\text{-}C(O)R\}L(CO)_2(PMe_3)]$, $[Mo\{\eta^2\text{-}C(O)R\}L(CO)(CNR')(PMe_3)]$ and $[Mo\{\eta^2\text{-}C(NR')R\}L(CO)_2(PMe_3)]$

	Analysis(%)[a]			IR data (Nujol)/cm^{-1}		^1H NMR (δ)			
Compound	C	H	N	ν_{CO} $\nu_{(CNR')}$	ν_{COR} $\nu_{[C(NR')R]}$	PMe_3[b]	R[c]	R'	L[c]
1	38.1	5.0	13.6	1940s	1600m	1.06	2.73 (s)		5.91 (t), 7.41, 7.50 (d, 2.1)
	(37.3)	(4.8)	(13.4)	1865s		(d, 9.6)			
2	43.3	6.0	11.8	1934s	1584m	1.13	1.04 (s, CMe_3),		5.92 (t), 7.45, 7.47 (d, 2.1)
	(43.0)	(5.9)	(11.8)	1848s		(d, 9.6)	3.41 (s, CH_2)		
3	43.0	6.3	11.9	1934s	1600m	1.26	2.85 (s)		2.22, 2.25, 5.60 (s)
	(43.0)	(5.9)	(11.8)	1837s		(d, 8.3)			
4	43.4	6.9	10.6	1934s	1562m	1.31	0.17 (s, $SiMe_3$),		2.26, 2.32, 5.63 (s)
	(43.9)	(6.6)	(10.3)	1835s		(d, 9.2)	3.30 (s, CH_2)		
5	47.3	7.1	9.9	1940s	1600w	1.29	1.09 (s, CMe_3),		2.25, 2.28, 5.62 (s)
	(47.5)	(6.8)	(10.6)	1848s		(d, 9.4)	3.62 (s, CH_2)		
6[d]	51.9	6.7	10.6	1810s	1560w	1.31	0.28 (s), 2.96, 3.76	2.25 (s, 2 Me),	2.19, 2.30, 2.34, 2.59, 5.70,
	(51.8)	(6.9)	(10.8)	2038s		(d, 8.7)	(d, 12.7, CH_2)	6.75 (m, Ph)	5.73 (s)
7	54.3	7.0	11.0	1820s	1567m	1.34	1.20 (s, CMe_3), 3.22,	4.25, 4.29 (J_{HH} =	2.16, 2.31, 2.34, 2.53, 5.67,
	(54.3)	(7.0)	(11.3)	2054s		(d, 8.7)	3.82 (d, 17.8, CH_2)	16.2, J_{HP} = 3.2), 7.0 (m, Ph)	5.71 (s)
8	53.1	7.8	11.7	1804s	1569m	1.41	1.28 (s, CMe_3), 3.39,	1.17, 1.38 (m), 1.60,	2.24, 3.31, 2.35, 2.58, 5.68,
	(53.0)	(7.8)	(11.5)	2081s		(d, 8.6)	3.94 (d, 17.7, CH_2)	3.35 (m)	5.73 (s)
9	55.0	7.1	10.7	1822s	1580m	1.32	1.20 (s, CMe_3), 3.42,	2.26 (s), 6.76 (AB_2)	2.17, 2.26, 2.27, 2.31, 5.64,
	(55.0)	(7.2)	(11.0)	2040s		(d, 8.8)	4.01 (d, 17.9, CH_2)	(J_{AB} = 7.7)	5.67 (s)
10	48.0	5.5	12.9	1932s	1696m	0.87	2.34 (s)	1.63 (s), 6.75 (AB_2)	5.87 (t), 7.52, 7.55 (d, 2.1)
	(48.4)	(5.6)	(13.4)	1800s		(d, 8.6)		(J_{AB} = 7.7)	
11	45.7	5.3	13.7	1937s	1720m	1.10	2.65 (s)	3.10 (s), 6.17 (m),	5.91, 7.45, 7.67 (d, 2.1)
	(45.9)	(5.2)	(13.4)	1816s		(d, 8.6)		6.44 (m)	
12	51.8	6.2	11.5	1928s	1716m	0.91	1.06 (s, CMe_3),	4.35 (s), 6.84 (m),	5.88 (t), 7.38, 7.51 (d, 2.1)
	(51.2)	(6.3)	(12.4)	1802s		(d, 8.5)	2.89 (s)	6.96 (m)	
13	49.8	7.2	12.6	1932s	1718m	1.17	1.15 (s, CMe_3),	0.47 (m), 0.86 (m),	6.00 (t), 7.51, 7.65 (d, 2.1)
	(49.8)	(7.1)	(12.6)	1810s		(d, 8.3)	2.90 (s)	1.31 (m), 3.27 (m)	
14	52.3	6.6	12.1	1924s	1684m	0.65	1.05 (s, CMe_3),	1.82 (s), 6.77 (s)	5.94 (t), 7.51, 7.80 (d, 2.1)
	(52.0)	(6.5)	(12.1)	1806s		(d, 8.3)	3.13 (s)		
15[e]	52.1	6.6	12.3	1932s	1691m	1.34	2.92 (s)	1.54 (s), 6.91 (s)	2.09, 2.24, 5.71 (s)
	(52.0)	(6.4)	(12.1)	1800s		(d, 9.2)			
16	49.9	5.6	12.2	1914s	1700m	1.40	2.93 (s)	3.10 (s), 6.17 (m),	2.01, 2.37, 5.65 (s)
	(49.7)	(6.0)	(12.1)	1811s		(d, 8.7)		6.42 (m)	
17	51.1	6.9	11.0			0.62	0.05 ($SiMe_3$),	2.08 (s), 6.78 (m)	2.21, 2.51, 5.70 (s)
	(51.8)	(6.9)	(10.8)			(d, 8.3)	3.10 (s)		

Solvent C_6D_6 unless otherwise stated. [a] Calculated values in parentheses. [b] J_{CP}/Hz in parentheses. [c] J_{HH}/Hz in parentheses. [d] NMR data in $C_6D_5CD_3$. [e] NMR data in $(CD_3)_2CO$.

solution changed from red to yellow (2 h). The solvent was then removed *in vacuo* and the residue extracted with light petroleum–Et_2O (1:1). Centrifugation and cooling at −15 °C afforded $[Mo\{\eta^2\text{-}C(O)Me\}\{H_2B(pz)_2\}(CO)_2(PMe_3)]$ **1**, as yellow crystals in 70% yield. Complexes **2–5** were similarly obtained as yellow crystals by carbonylation of the corresponding monocarbonyl derivatives.[5] They required, however, longer reaction times or alternatively higher CO pressures (3–4 atm, *ca.* 3×10^{-5}–4×10^{-5} Pa), although in the latter case the reaction yields were somewhat lower.

$[Mo\{\eta^2\text{-}C(O)R\}L(CO)(CNR')(PMe_3)]$ (structure B). The complex $[Mo\{\eta^2\text{-}C(O)CH_2CMe_3\}\{H_2B(dmpz)_2\}(CO)(PMe_3)_2]$[5] (0.58 g, 1 mmol) was dissolved in thf (60 cm^3) at room temperature and neat $CNCH_2Ph$ (0.1 cm^3, 1 mmol) was added directly to the stirred solution. After 15 min the reaction mixture changed from red to dark yellow. The solvent was removed *in vacuo* to produce a brown solid, which was crystallized from light petroleum–Et_2O (2:1) to afford orange crystals of **7** in 60% yield.

Adding the appropriate CNR' ligand to $[Mo\{\eta^2\text{-}C(O)CH_2CMe_3\}\{H_2B(dmpz)_2\}(CO)(PMe_3)_2]$ allowed the preparation of complexes **8** and **9** by the same procedure as orange crystals. They were isolated by crystallization from light petroleum–Et_2O (1:1) in 78% yield (**8**) and from Et_2O in 63% yield (**9**). The synthesis of the CH_2SiMe_3 derivative, **6**, was accomplished by the above procedure using $[Mo\{\eta^2\text{-}C(O)CH_2SiMe_3\}\{H_2B(dmpz)_2\}(CO)(PMe_3)_2]$[5] as the starting material, but in order to avoid further reactivity temperatures below 5 °C were, however, required during the work-up process. It was isolated as orange crystals in 85% yield.

$[Mo\{\eta^2\text{-}C(NR')R\}L(CO)_2(PMe_3)]$ (structure C). The compound $CNC_6H_3Me_2$-2,6 (0.13 g, 1 mmol) was dissolved in thf (40 cm^3) at room temperature and $[Mo\{\eta^2\text{-}C(O)CH_2CMe_3\}\{H_2B(pz)_2\}(CO)(PMe_3)_2]$[5] added. The resulting mixture was stirred for 1–2 h at 60 °C, the solvent was removed under reduced pressure and the residue extracted with light petroleum. Centrifugation and cooling at −35 °C afforded **14** as orange crystals in 41% yield.

Using the appropriate molybdenum complex[5] and CNR' the following compounds were obtained by the above procedure: **10** (50), **11** (70), **12** (54), **13** (57), **15** (78), **16** (51) and **17** (90% yield). They were isolated as orange crystalline solids from light petroleum with the only exception of the less-soluble derivative **12**, which required light petroleum–Et_2O (3:1).

Kinetic studies of the isomerization of the dihaptoacyl $[Mo\{\eta^2\text{-}C(O)CH_2SiMe_3\}\{H_2B(dmpz)_2\}(CNR')(CO)(PMe_3)]$ (R' = Bu^t or $C_6H_3Me_2$-2,6) into the corresponding iminoacyl $[Mo\{\eta^2\text{-}C(NR')CH_2SiMe_3\}\{H_2B(dmpz)_2\}(CO)_2(PMe_3)]$

In both cases, the disappearance of the acyl isomer was monitored at 24 °C by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy for a

Table 2 The ^{31}P-{^1H} and ^{13}C-{^1H} NMR data for compounds **1**–**17**

Compound	^{31}P-{^1H} (δ)	^{13}C-{^1H} (δ)				
		PMe_3[a]	R	N–N	R'[a]	CX/C(X)R[b]
1	12.1 (s)	16.6 (d, 30)	31.2 (s)	105.0, 136.4, 143.3 (s)		230.4 (d, 17, CO) 254.0 (d, 13, *C*OR)
2	10.2 (s)	17.4 (d, 29)	29.5 (s, C*Me*$_3$), 32.8 (s, *C*Me$_3$), 60.2 (s, CH_2)	105.2, 136.5, 143.4 (s)		231.2 (d, 18, CO) 255.8 (d, 12, *C*OR)
3	15.3 (s)	17.8 (d, 33)	32.4 (s)	12.6, 14.0 (s, Me), 106.8, (s, CH), 144.9, 150.5 (s, *C*Me)		230.4 (d, 22, CO) 262.0 (d, 11, *C*OR)
4	12.1 (s)	17.2 (d, 31)	−0.9 (s, $SiMe_3$), 40.0 (s, CH_2)	14.4, 12.7 (s, Me), 106.3 (s, CH), 149.8, 143.5 (s, *C*Me)		231.6 (d, 21, CO) 258.1 (d, 10, *C*OR)
5	13.0 (s)	17.3 (d, 31)	29.1 (s, C*Me*$_3$), 31.6 (s, *C*Me$_3$), 60.9 (s, CH_2)	12.6, 14.1 (s, Me), 106.3 (s, CH), 143.4, 149.7 (s, *C*Me)		230.4 (d, 22, CO) 260.8 (d, 10, *C*OR)
6	11.2 (s)	17.1 (d, 29)	−0.6 (s, $SiMe_3$), 39.0 (s, CH_2)	12.8, 12.9, 14.8, 14.9 (s, Me), 106.3, 105.9 (s, CH), 143.0, 143.4, 150.4, 150.8 (s, *C*Me)	18.6 (s, $C_6H_3Me_2$), 126.0, 129.3 (s, 3CH of $C_6H_3Me_2$), 132.6 (s, 2*C*CH_3 of $C_6H_3Me_2$)	
7	7.5 (s)	17.6 (d, 28)	29.4 (s, C*Me*$_3$), 31.6 (s, *C*Me$_3$), 60.2 (s, CH_2)	12.6, 12.8, 14.2, 14.8 (s, Me), 105.9, 106.2 (s, CH), 142.9, 143.2, 148.7, 150.7 (s, *C*Me)	48.5 (s, *C*H_2Ph), 127.0 (s, 2CH of Ph), 128.0 (s, CH of Ph), 128.7 (s, 2CH of Ph), 134.6 (s, C_{ipso})	192.2 (d, 26, *C*NR') 233.3 (d, 20, CO) 268.3 (d, 13, *C*OR)
8[b]	13.7 (s)	17.5 (d, 28)	29.5 (s, C*Me*$_3$), 31.6 (s, *C*Me$_3$), 60.1 (s, CH_2)	12.6, 12.8, 14.3, 14.7 (s, Me), 105.8, 106.3 (s, CH), 142.8, 143.1, 148.5, 150.8 (s, *C*Me)	23.5 (s, 2CH_2 of C_6H_{11}), 24.7 (CH_2 of C_6H_{11}), 33.7 (s, 2CH_2 of C_6H_{11}), 54.6 (s, CH of C_6H_{11})	183.6 (d, 27, *C*NR') 233.3 (d, 21, CO) 269.5 (d, 13, *C*OR)
9	12.2 (s)	17.9 (d, 29)	29.6 (s, C*Me*$_3$), 32.0 (s, *C*Me$_3$), 61.0 (s, CH_2)	13.0, 13.1, 14.6, 14.8 (s, Me), 106.2, 106.5 (s, CH), 143.2, 143.5, 149.1, 150.8 (s, *C*Me)	18.2 (s, 2CH_3 of $C_6H_3Me_2$), 126.1 (s, CH of $C_6H_3Me_2$), 128.4 (s, 2CH of $C_6H_3Me_2$), 130.6 (s, C_{ipso}), 132.7 (s, *C*CH_3 of $C_6H_3Me_2$)	199.8 (d, 27, *C*NR') 232.7 (d, 21, CO) 266.7 (d, 12, *C*OR)
10	3.2 (s)	16.1 (d, 25)	21.3 (s)	104.7, 136.4, 143.9 (s, CH)	17.6 (s, 2CH_3 of $C_6H_3Me_2$), 125.2 (s, CH of $C_6H_3Me_2$), 128.0 (s, 2CH of $C_6H_3Me_2$), 130.2 (s, *C*CH_3 of $C_6H_3Me_2$)	206.7 (d, 11, *C*OR) 234.8 (d, 17, CO)
11	4.0 (s)	16.7 (d, 27)	21.3 (s)	104.7, 136.1, 143.7 (s, CH)	54.4 (s, *C*H_3OPh), 114.3, 123.2 (s, 2CH of Ph), 132.2 (s, C_{ipso}), 157.5 (s, *C*OMe)	202.2 [d, 12, *C*(NR')R] 236.1 (d, 19, CO)
12	2.2 (s)	16.4 (d, 26)	30.0 (s, C*Me*$_3$), 33.6 (s, *C*Me$_3$), 44.7 (s, CH_2)	104.3, 136.1, 143.7 (s, CH)	52.3 (d, 3, *C*H_2Ph), 126.8 (s, 2CH of Ph), 128.2 (s, 3CH of Ph), 135.8 (s, C_{ipso})	201.3 [d, 12, *C*(NR')R] 238.3 (d, 18, CO)
13	4.5 (s)	17.2 (d, 26)	30.1 (s, C*Me*$_3$), 32.8 (s, *C*Me$_3$), 44.2 (s, CH_2)	104.3, 136.0, 144.1 (s, CH)	24.7 (s, 2CH_2 of C_6H_{11}), 25.1 (s, CH_2 of C_6H_{11}), 31.4 (s, 2CH_2 of C_6H_{11}), 57.6 (s, 3CH of C_6H_{11})	193.7 [d, 11, *C*(NR')R] 238.6 (d, 19, CO)
14	0.9 (s)	15.5 (d, 24)	29.9 (s, C*Me*$_3$), 33.9 (s, *C*Me$_3$), 47.4 (s, CH_2)	104.6, 136.7, 144.2 (s, CH)	18.2 (s, 2CH_3 of $C_6H_3Me_2$), 125.3 (s, CH of $C_6H_3Me_2$), 128.0 (s, 2CH of $C_6H_3Me_2$), 129.9 (s, *C*CH_3 of $C_6H_3Me_2$)	206.5 [d, 11, *C*(NR')R] 238.0 (d, 17, CO)
15[c]	12.4 (s)	17.5 (d, 28)	23.8 (s)	13.6, 15.7 (s, Me), 107.3 (s, CH), 145.2, 151.6 (s, *C*Me)	17.9 (s, 2CH_3 of $C_6H_3Me_2$), 125.9 (s, CH of $C_6H_3Me_2$), 129.1 (s, 2CH of $C_6H_3Me_2$), 131.2 (s, 2*C*CH_3 of $C_6H_3Me_2$)	211.6 [d, 12, *C*(NR')R] 236.5 (d, 20, CO)
16	7.6 (s)	17.7 (d, 28)	23.2 (s)	14.5, 13.0 (s, Me), 105.8 (s, CH), 143.9, 149.2 (s, *C*Me)	54.3 (s, CH_3O), 114.6, 122.6 (s, 2CH of Ph), 131.8 (s, C_{ipso}), 157.0 (*C*OMe)	205.5 [d, 8, *C*(NR')R] 235.8 (d, 20, CO)
17	1.4 (s)	16.0 (d, 23)	−0.7 (s, $SiMe_3$), 28.7 (s, CH_2)	13.6, 16.6 (s, Me), 106.9 (S, CH), 145.7, 151.7 (s, *C*Me)	18.4 (s, 2CH_3 of $C_6H_3Me_2$), 124.9 (s, CH of $C_6H_3Me_2$), 128.5 (s, 2CH of $C_6H_3Me_2$), 130.1 (s, 2*C*CH_3 of $C_6H_3Me_2$)	204.8 [d, 12, *C*(NR')R] 240.0 (d, 18, CO)

Solvent C_6D_6 unless otherwise stated. [a] J_{CP} in parentheses. [b] In $C_6D_5CD_3$. [c] In $(CD_3)_2CO$.

period of about four half-lives. The two reactions were well behaved and produced the iminoacyl isomers as the only detectable products. Duplicate experiments were performed in both cases. In a typical experiment, a solution of complex **6** in C_6D_6 (around 0.08 mol dm^{-3}) was transferred under N_2 into a 5 mm NMR tube which was then frozen and degassed. In order to avoid possible interference from an internal reference, a capillary containing a solution of PPh_3 in acetone (around 0.04 mol dm^{-3}) was introduced inside the NMR tube and employed as an external standard. The tube was sealed and placed into a NMR probe at 24 °C (uncertainty ±0.1 °C) and its ^{31}P-{^1H} NMR spectrum recorded on a Bruker AMX-500 spectrometer. In each experiment the acquisition was performed using an interscan delay of about five times the slowest relaxation time of the ^{31}P nuclei.

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