Heterobimetallics from uranium or neodymium and d transition metals

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Abstract

Syntheses of heterobi- and trinuclear complexes containing both a d metal (Mo, W, Ru, Rh) and an f metal (U^{IV} or Nd^{III}) in close proximity but without a direct metal–metal bond were performed using anionic alkoxyphosphines, $HO(CH_2)_nPPh_2$ ($n = 0$ or 1), cyclopentadienylphosphines, $C_5R_4PR'_2$ ($R \equiv H$ or Me; $R' \equiv Ph$ or Me), or neutral diphosphine monoxide, $OPPh_2CH_2PPh_2$, as heterodifunctional bridging ligands.

1. Introduction

A large number of early–late heterobimetallic complexes have been reported [1–3] but, despite the scarcity of significant catalytically active species [4, 5], the chemistry of these compounds remains of great interest.

The synthesis of heterobi- and polynuclear molecules containing both a uranium atom [6–8] or a neodymium atom as modelling U^{III} and a late transition metal (palladium, platinum, rhodium or ruthenium) strongly bonded in close proximity but without a direct metal–metal bond represents an area that we have recently investigated. Two kinds of difunctional bridging ligands are used to build such complexes: anionic, the classical cyclopentadienylphosphido ligand $[C_5R_4PR'_2]^-$ ($R \equiv H$ or CH_3; $R' \equiv C_6H_5$ or CH_3) and the less common alkoxyphosphido group $[O(CH_2)_nPPh_2]^-$ ($n = 0$ or 1) [9, 10]; neutral, the diphosphine monoxides $OPPh_2CHRPPh_2$ ($R \equiv H$ or *n*-propyl) [11, 12].

2. Results and discussion

2.1. Heterometallics from uranium alkoxyphosphines

The most catalytically active actinide species are the bispentamethylcyclopentadienides [13, 14] and related bridged hydrides [12] synthesized by Marks and co-workers (Scheme 1). Among these complexes, the alkoxyhydrides, $(C_5Me_5)_2U(OR)H$, exhibit good stability and appear to be interesting olefin polymerization catalysts [14]. Such alkoxyhydrides with $OR \equiv O(CH_2)PPh_2$ could be used to build heterobimetallics.
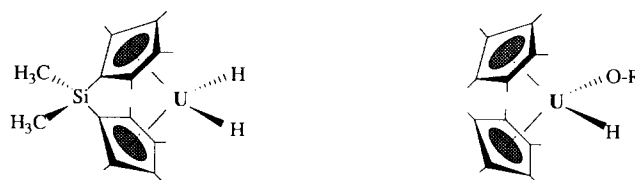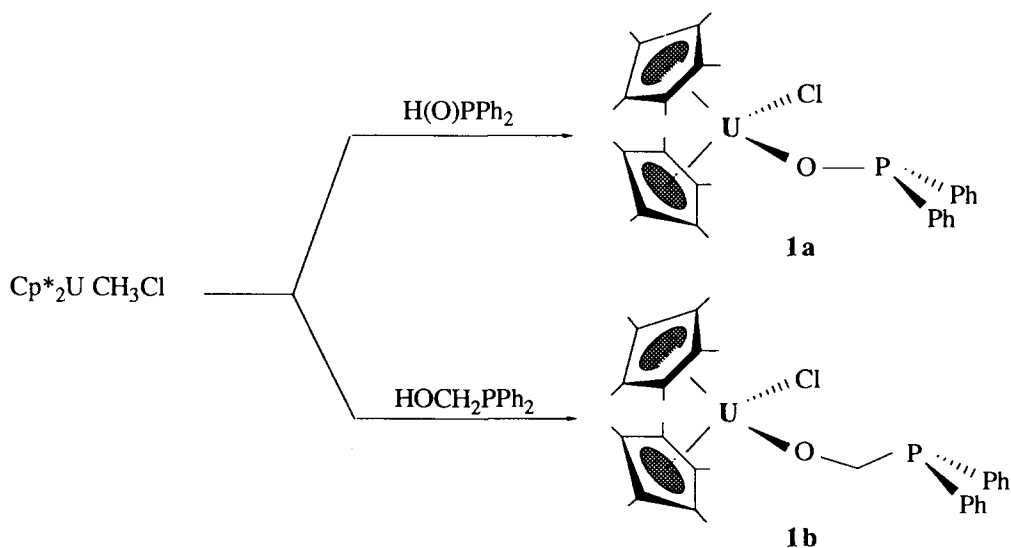

Scheme 1.

The syntheses of the uranoalkoxyphosphines **1a**, **1b**, **2a**, **2b**, **3a** and **3b** were conducted from alkoxyphosphines $HO(CH_2)_nPPh_2$ with $n = 0$ (**a**) and $n = 1$ (**b**) and alkyl or diethylamido uranium derivatives or from the potassium salt $KOPPh_2$ and $(C_5H_5)_3UCl$ according to Schemes 2–4. The ^1H and ^{31}P nuclear magnetic resonance (NMR) data of these complexes are reported in Table 1.

Bimetallic species were obtained from the chloride complexes instead of the hydrides because of the very high reactivity of the uranium hydrides. In a first step, we used the ubiquitous $(NBD)M(CO)_4$ (NBD, norbornadiene; $M \equiv Mo$, W) to model the complexation of a d metal on the uranium alkoxyphosphines.

The tri- or binuclear molecules of general formula $Mo(CO)_4(PPh_2[U])_2$ **4b**, **6a**, **6b** and $M(CO)_4(PPh_2)_2[U]$ ($M \equiv Mo$, W) **5a**, **5a'**, **5b** were obtained by reaction of stoichiometric amounts of $(NBD)M(CO)_4$ with compounds **1–3** in toluene solution (Scheme 5). All these complexes exhibit a *cis* configuration around the molybdenum (or tungsten) centre (Table 2). On heating, **6a** isomerizes into its *trans* isomer. NMR data are reported in Table 3.

The sterically less hindered $-OCH_2PPh_2$ complexes **1b–3b** react significantly more rapidly than the cor-
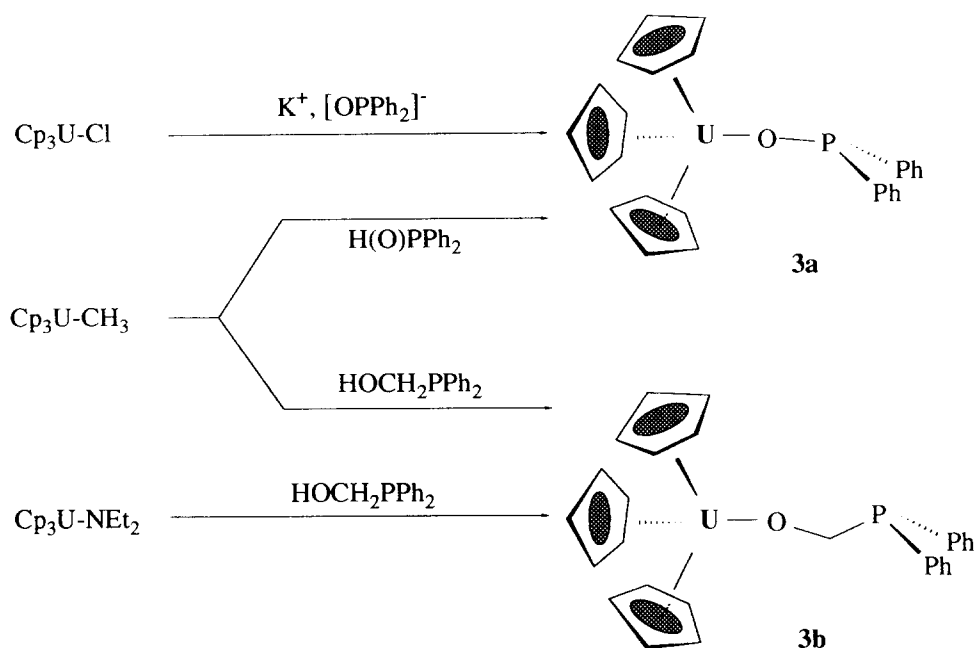
Scheme 2.
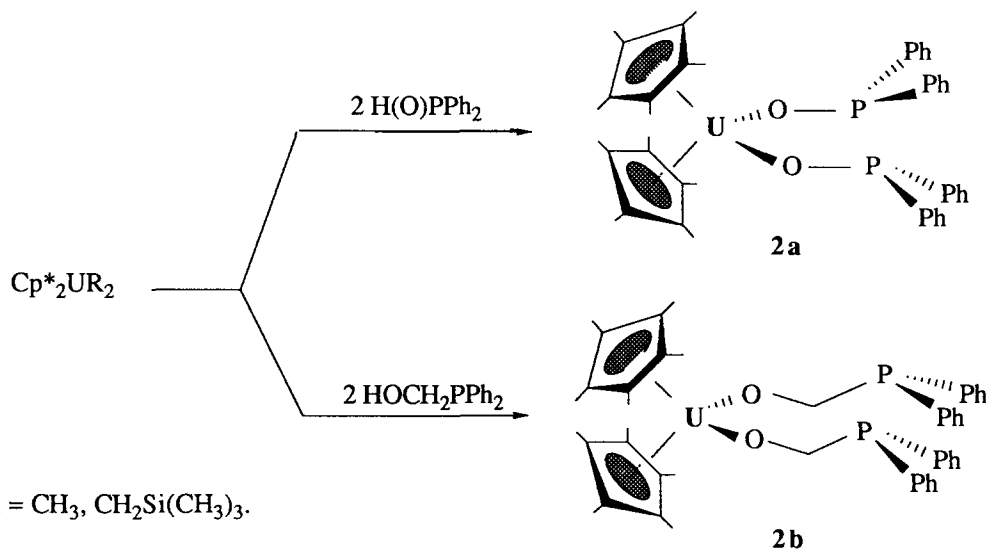
R = CH₃, CH₂Si(CH₃)₃.

Scheme 3.

responding OPPh₂ species 1a–3a. Moreover, from 1a, we were unable to obtain the trinuclear complex analogous to 4b, but 1a reacts easily with Mo(CO)₅ to give 7a.

An interesting feature was the comparison of the ^{31}P NMR data of the heterometallic complexes and of their uranoalkoxyphosphine precursors. As can be seen in Fig. 1, all heterometallics containing the OPPh₂ ligand exhibit abnormal behaviour: the phosphorus signal is shifted at higher fields than in the starting complex. It is well known that phosphine coordination on a d metal leads to a deshielding of the phosphorus signal of ca. 50 ppm. This has also been observed for uraniumcyclopentadienylphosphines [6–8]. This suggests that the starting "alkoxyphosphines" 1a, 2a, 3a would

not be "pure" alkoxides (A in Scheme 6) but were more conveniently represented as (B in Scheme 6) involving a direct uranium–phosphorus interaction which disappears in the bimetallics. This should be compared with the carbenoid form reported for the inserted products of CO into the actinide–carbon bonds [16].

The syntheses of uranium–ruthenium bimetallics, monitored by NMR, were attempted in two ways: exchange of PPh₃ groups of ruthenium complexes by the uranium alkoxyphosphines 1–3; reaction of the new rutheno alkoxyphosphines 8 (Scheme 7) and H₂Ru(PPh₂CH₂OH)₂(PPh₃)₂, 9, obtained from RuCl₃ (8) and H₂Ru(PPh₃)₄ (9), with alkyluranium species. In some cases, the formation of the expected compounds

Scheme 4.

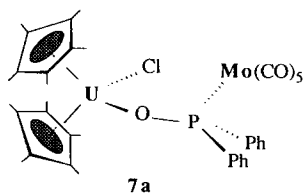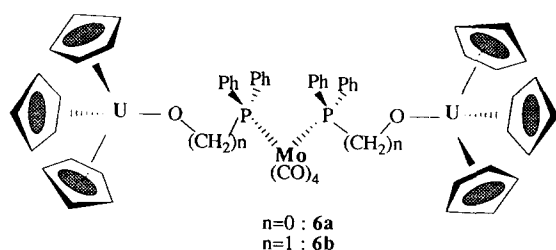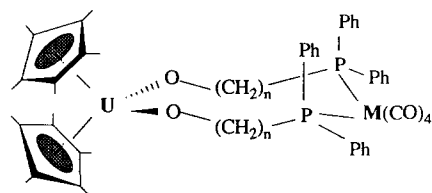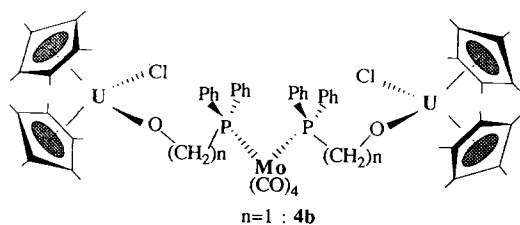TABLE 1. ^{1}H and ^{31}P nuclear magnetic resonance data of the uranium alkoxyphosphines 1–3

Compound	^{31}P	C_5R_5	$-CH_2-$	$-C_6H_5$		
				o	m	p
1a	+154	+8.58 (s, 30H)	–	+1.62 (t, 4H)	+5.91 (t, 4H)	+7.14 (t, 2H)
1b	+49.7	+5.45 (s, 30H)	+68.3 (s, 2H)	+11.2 (t, 4H)	+7.35 (t, 4H)	+7.12 (t, 2H)
2a	+129	+4.71 (s, 30H)	–	−3.25 (t, 8H)	+4.65 (t, 8H)	+5.55 (t, 4H)
2b	−18.7	+0.66 (s, 30H)	+11.9 (s, 4H)	+4.5 (t, 8H)	+6.1 (t, 8H)	+6.3 (t, 4H)
3a	+123	−7.72 (s, 15H)	–	−2.47 (t, 4H)	+4.80 (t, 4H)	+5.28 (t, 2H)
3b	−4.25	−14.7 (s, 15H)	+35.6 (s, 2H)	+8.06 (t, 4H)	+6.66 (t, 4H)	+6.74 (t, 2H)

seemed to occur, but they were unstable in solution and complex mixtures were finally obtained. One of the reasons for this failure seems to be the easy ligand scrambling between the linked metal centres (as observed by Wolczanski and coworkers in the synthesis of Zr–Rh compounds [17]).

Thus the synthesis of such uranium–ruthenium bimetallics appears to be much more difficult than that of uranium–molybdenum species. Nevertheless, the bimetallic 10 (Scheme 8) (^{1}H NMR, δ (ppm) = −25 (RuH), −9.2 (CpU), −3.9, −3.1 (o-Ph), 2.4 (CpRu), 4.0, 4.9 (m-Ph), 5.0, 5.3 (p-Ph); ^{31}P NMR, δ = 154 ppm)

has been obtained from Cp_3UOPPh_2 3a and $RuH_2(PPh_3)_4$ (the latter was selected for its high catalytic performances [18]).

Until now, it has not been established whether the Cp–Ru moiety is provided by exchange from a part of the starting triscyclopentadienyluranium 3a or from free cyclopentadiene [19] resulting from a partial hydrolysis of 3a. We found [20] that a fast quantitative chlorination of $RuH_2(PPh_3)_4$ took place by exchange with early transition metal chlorides (Cp_2MCl_2, M = Ti, Zr) or with f metal chlorides (UCl_4, $NdCl_3$). $RuHCl(PPh_3)_3$ so obtained was found to be 300–1000 times more

n=1 : 4b

n=0 , M=Mo : 5a
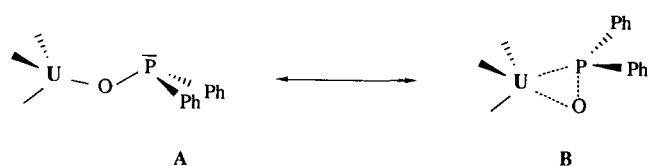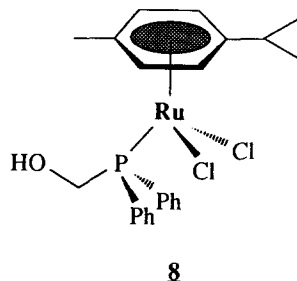   M=W : 5'a
n=1 , M=Mo : 5b

Scheme 6.

8

Scheme 7.

n=0 : 6a
n=1 : 6b

10

Scheme 8.

7a

Scheme 5.

TABLE 2. IR data of the bimetallic species **4b–7a**

Compound	ν_{CO} (cm^{-1})
Mo(CO)$_4$NBD	2040, 1954, 1910, 1885
cis-(HOCH$_2$PPh$_2$)$_2$Mo(CO)$_4$	2020, 1925, 1904, 1894
4b: *cis*-[Cp$_2^*$UCl(OCH$_2$PPh$_2$)]$_2$Mo(CO)$_4$	2020, 1925, 1905, 1895
5a: *cis*-Cp$_2^*$U(OPPh$_2$)$_2$Mo(CO)$_4$	2020, 1925, 1905, 1890
5a': *cis*-Cp$_2^*$U(OPPh$_2$)$_2$W(CO)$_4$	2020, 1939, 1903, 1899
5b: *cis*-Cp$_2^*$U(OCH$_2$PPh$_2$)$_2$Mo(CO)$_4$	2020, 1925, 1904, 1894
6b: *cis*-[Cp$_3$UOCH$_2$PPh$_2$]$_2$Mo(CO)$_4$	2021, 1924, 1904, 1890
7a: Cp$_2^*$UCl(OPPh$_2$)MO(CO)$_5$	2072, 1945, 1903

Scheme 9.

2.2. Heterobimetallics from neodymium derivatives

We intended to synthesize heterometallics in which a strong anionic difunctional ligand should maintain the two metal centres in close proximity whereas a weaker neutral ligand could provide, by coordination–decoordination steps, both creation or protection of vacant active sites. The "strong ligating" ligand could be the classical phosphinocyclopentadienide ring (bearing PPh$_2$ or the more basic PMe$_2$ group); the weaker
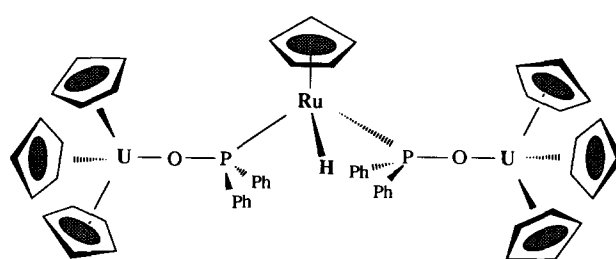
active for the hydrogenation of internal olefins (even under low pressure, 0.5–0.05 atm) than previously described [21].

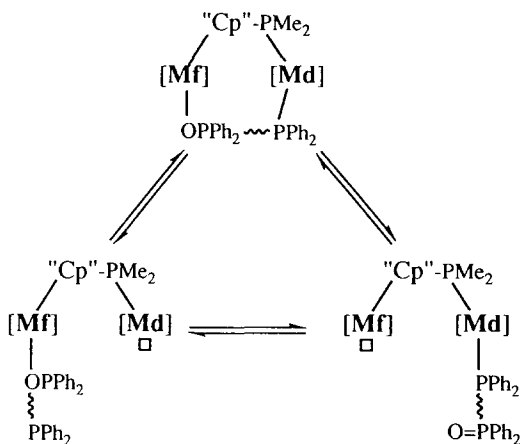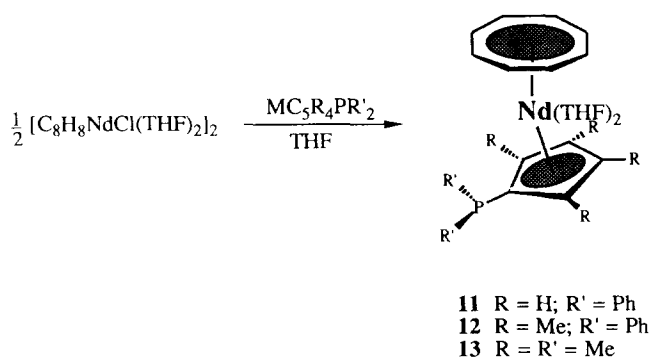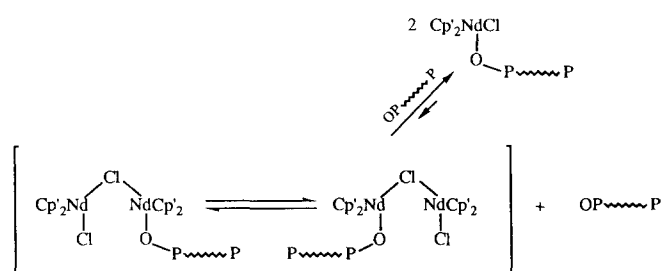$\frac{1}{2}$ [C₈H₈NdCl(THF)₂]₂ $\xrightarrow[\text{THF}]{\text{MC}_5\text{R}_4\text{PR}'_2}$

$\frac{1}{2}$ [C$_8$H$_8$NdCl(THF)$_2$]$_2$ $\xrightarrow[\text{THF}]{\text{MC}_5\text{R}_4\text{PR}'_2}$

11 R = H; R' = Ph
12 R = Me; R' = Ph
13 R = R' = Me

Scheme 10.

Scheme 11.

neutral heterodifunctional ligand ought to be a diphosphine monoxide (dppmo) (Scheme 9). These ligands were tested on Nd^{III} instead of U^{III}. These two ions have the same ionic radii and some analogous organometallic complexes have been described [22, 23]. Enhanced stability and crystallinity were expected in the neodymium series. A cyclooctatetraenide ring was used instead of two Cp rings to favour the further coordination of dppmo. Mixed lanthanide cyclopentadienyl–cyclooctatetraenyl complexes have been described since the mid-1970s [24, 25] and this combination of ring systems

on a U^{III} metal centre has been reported recently [26, 27].

The new organolanthanides (COT)Nd(C$_5$R$_4$PR$'_2$) (COT, cyclooctatetraenide ring; R ≡ H or CH$_3$, R' ≡ C$_6$H$_5$ or CH$_3$) 11, 12, 13 were synthesized from [COTNdCl(THF)$_2$]$_2$ [28] according to Scheme 10. NMR data are listed in Table 4. These exceedingly air- and moisture-sensitive complexes were obtained in good yields. Crystals were obtained; they were unfortunately not suitable for X-ray structural analysis. It has been impossible to obtain convenient elemental analyses, whereas this was possible for the analogous samarium complexes [29]. It is well known that unlike the organometallic complexes of the late lanthanides, the early lanthanide complexes are very rarely characterized by elemental analysis [30]. In the recently published results for (COT)U^{III}(C$_5$Me$_5$)(Me$_2$bpy) [26, 27], the bond lengths and angles are quite similar to those found in the early lanthanide complex (COT)-Sm(C$_5$H$_4$PPh$_2$)(THF)$_2$ [29].

From 11 and (C$_5$H$_5$)Rh(CO)$_2$, the formation of the expected complex (COT)Nd(C$_5$H$_4$PPh$_2$)Rh(C$_5$H$_5$)(CO) 14 was established by ^{31}P NMR: $\delta = -48$ ppm, $J_{P-Rh} = 178$ Hz. Compound 12 did not react whereas 13 led to a complex mixture.

The coordination of the neutral dppmo (OPPh$_2$CH$_2$PPh$_2$) was first studied (by NMR ^{1}H and ^{31}P) on the more stable [(C$_5$H$_4$tBu)$_2$NdCl]$_2$ [10, 30]. Only one dppmo ligand was reversibly coordinated per metal unit. The last step of the opening of the bridged dimer is shown in Scheme 11 (Cp', C$_5$H$_4$tBu). In the same way, ^{31}P NMR established the coordination of one dppmo ligand on (COT)NdCl. The reaction of this adduct with (NBD)Mo(CO)$_4$ affords the trinuclear species [(COT)NdCl(dppmo)]$_2$Mo(CO)$_4$.

TABLE 3. ^{1}H and ^{31}P nuclear magnetic resonance data of the bimetallics 4b–7a

Compound	^{31}P	C$_5$R$_5$	–CH$_2$–	–C$_6$H$_5$		
				o	m	p
4b	+87	+7.0	+60.8	+10.3	+7.05	+7.04
5a	+120	+5.6		−1.87	+4.4	+5.3
5a'	+95 ($J_{P-W} = 134$ Hz)	+5.9		−1.94	+4.4	+5.3
5b	+42.6	+0.3	+16.7	+7.1	+6.5	+6.5
6a (cis)	+85	−6.1		−6.1	+5.2	+5.9
6a (trans)	+57	−5.2		−6.4	+5.1	+5.8
6b	+29.9	−12.3	+17.0	+5.7	+4.0	+6.3
7a	+96	+13.9		−0.6	+7.2	+8.4

bimetallics

Δ   Mo(CO)₄
*   Mo(CO)₅
o   W(CO)₄

Δ $* \ o \ \Delta \bigwedge \Delta$ $\Delta\Delta$ Δ

Cp*₂UCl(OPPh₂)

Cp*₂U(OPPh₂)₂
Cp₃UOPPh₂

Cp*₂UCl(OCH₂PPh₂)

Cp₃UOCH₂PPh₂
HOCH₂PPh₂
Cp*₂U(OCH₂PPh₂)₂
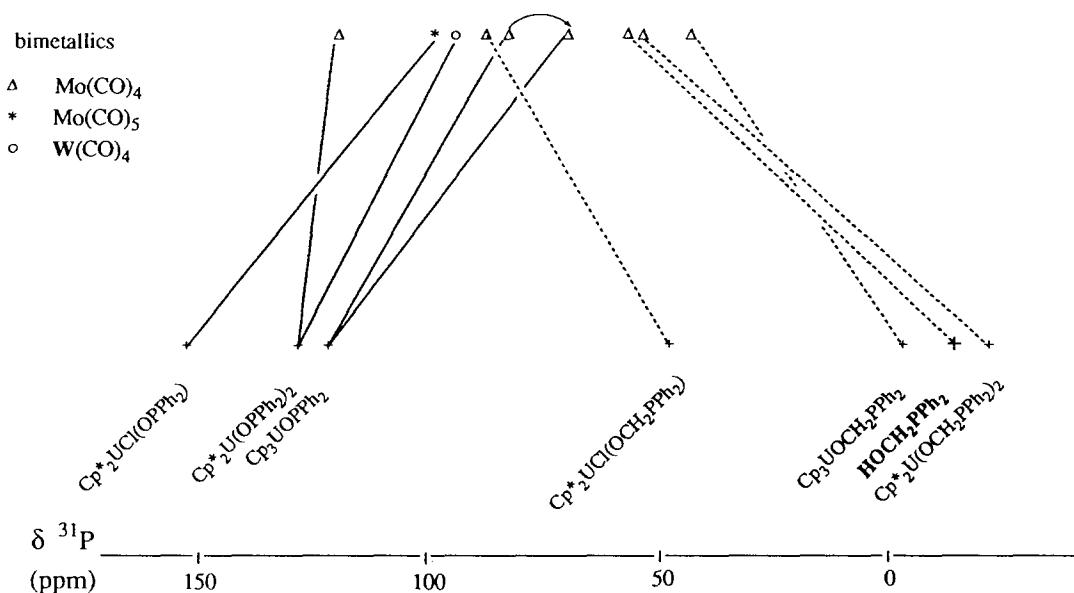
δ ³¹P
(ppm)   150   100   50   0

Fig. 1. Variations in the ³¹P chemical shifts after coordination of the d metal on the uranium alkoxyphosphines.

TABLE 4. Nuclear magnetic resonance data of neodymium complexes 11, 12 and 13

Compound (solvent)	¹Hª							³¹P
	R≡H	R≡Me	R′≡C₆H₅			R′≡Me	COT	
			p-Ph	m-Ph	o-Ph			
11 (C₆D₆)	9.4ᵇ (>100)		5.72 (15)	5.27 (15)	1.54 (20)		−14.26 (70)	–
12 (C₇D₈)		8.92 (50)	7.62 (40)	5.93 (15)	5.32 (15)	−2.97 (20)		−14.75 (120)	−92.8
13 (C₇D₈+2 THFᶜ)	9.97 (40)	7.44 (40)				−10.81 (25)	−15.58 (90)	−127.1

ªValues of $\omega_{1/2}$ (Hz) are given in parentheses.
ᵇThe second Cp signal is masked.
ᶜTHF, tetrahydrofuran.

Until now doubly bonded heterometallics have not been obtained from neodymium and, although the best results are expected in the samarium series, we turn now our attention to the U^{III} chemistry. The very easy sodium amalgam reduction of $(C_5H_4PPh_2)_2U(BH_4)_2$ affords the new stable $[(C_5H_4PPh_2)_2U^{III}(BH_4)]_2$ [31]. This compound could be a precursor in the synthesis of d metal bridged biscyclopentadienyluranium(III) hydrides by coordination of the two phosphorus atoms on the same d metal [6, 8, 32–34].

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