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Early–late heterobimetallic chemistry: reaction of a stable carbene adduct of $[(C_4Me_4P)_2Yb]_n$ with ruthenium hydrides, transient formation of a bimetallic Yb–Ru hydride and synthesis of $(C_4Me_4P)RuH(PPh_3)_2$

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Summary — The new complexes $(tmp)_2Yb(carbene)$ **1a** and **1b** (tmp = C_4Me_4P and carbene = $C_2Me_2(N^iPr)_2C$ and $C_2Me_2(NMe_2C)$) have been synthesized from $[(tmp)_2Yb]_n$ and characterized by elemental analysis and by NMR (^1H, ^{31}P). Complexes **1a** and **1b** are not stable in THF. Complex **1a** reacts in benzene-d_6 with $RuH_4(PPh_3)_3$ to give the moderately stable heterobimetallic dihydride $(PPh_3)_2RuH_2{-}\mu(tmp)_2{-}Yb(carbene)$ **2a** and with $RuHCl(PPh_3)_3$ to give $(tmp)RuH(PPh_3)_2$ **4**. The formation of the analogous complex **2b** is not observed when **1b** is allowed to react with $RuH_4(PPh_3)_3$. The nature of **2a** is established by NMR. After two days at room temperature, **2a** is transformed into $C_2Me_2(N^iPr)_2CH_2$ **3a**, **4** and $(tmp)RuH(PPh_3)(carbene)$ **4′**. Complex **4** was obtained analytically pure from $RuHCl(PPh_3)_3$ and tmpK whereas a mixture of **4** and **4′** is obtained after addition of an excess of $C_2Me_2(N^iPr)_2CH_2$ to a solution of **4**.

lanthanide / heterobimetallic / early–late complex / carbene adduct / ytterbium / ruthenium

Résumé — Chimie des hétérobimétalliques «early–late» : réaction d'un adduit carbène stable de $[(C_4Me_4P)_2Yb]_n$ avec un hydrure de ruthénium. Formation d'un dihydrure bimétallique ytterbium–ruthénium et synthèse de $(C_4Me_4P)RuH(PPh_3)_2$. Les complexes $(tmp)_2Yb(carbène)$ **1a** et **1b** (tmp = C_4Me_4P, carbène = $C_2Me_2(N^iPr)_2C$ et $C_2Me_2(NMe)_2C$) ont été synthétisés à partir de $[(tmp)_2Yb]_n$ et caractérisés par analyse élémentaire et par RMN ^1H et ^{31}P. Les complexes **1a** et **1b** ne sont pas stables dans le THF; **1a** réagit dans le benzène-d_6 avec $RuH_4(PPh_3)_3$ pour former le bimétallique $(PPh_3)_2RuH_2{-}\mu(tmp)_2{-}Yb(carbène)$ **2a** et avec $RuHCl(PPh_3)_3$ pour donner $(tmp)RuH(PPh_3)_2$ **4**. La formation du complexe bimétallique homologue **2b**, à partir de **1b** et de $RuH_4(PPh_3)_3$, n'est pas observée. Le complexe **2a** est modérément stable en solution. Après 48 h, il disparaît du milieu réactionnel et on observe la formation de $C_2Me_2(N^iPr)_2CH_2$ **3a**, **4** et $(tmp)RuH(PPh_3)(carbène)$ **4′**. Le composé **4** a été obtenu analytiquement pur à partir de $RuHCl(PPh_3)_3$ et tmpK. Un mélange de **4** et **4′** est obtenu quand on ajoute un excès de carbène $C_2Me_2(N^iPr)_2C$ à une solution de **4**.

lanthanide / hétérobimétallique / complexe early–late / adduit carbène / ytterbium / ruthénium

Introduction

The synthesis and the chemistry of early–late transition-metal bimetallic hydrides [1] is currently receiving considerable attention. The impetus for this interest is the synergistic catalytic activity expected for an association of two metallic centers, each one alone showing catalytic properties [2]. A few examples of such cooperative effects have recently been described [3].

To achieve this goal, it is necessary to synthesize strongly bridged bimetallics that will remain bridged throughout the catalytic process. In a large number of complexes which are able to meet this requirement, the two metal centers are bridged by phosphino groups [4]; recently, we have described the synthesis of new early–late heterobimetallic dihydrides in which a $RuH_2(PPh_3)_2$ moiety is associated to a chelating bisphosphino metalloligand: $(PMe_2C_5Me_4)_2ZrCl_2$ [5], or to a chelating bis-tetramethylphospholyl (tmp) moiety: $(tmp)_2MX_2$ with MX_2 = $ZrCl_2$, UCl_2, $U(BH_4)_2$ or $Yb(THF)_2$ [6].

Unfortunately, this latter ytterbium compound was only soluble in THF when synthesized in this solvent. Isolated and analyzed crystals were obtained from a benzene–THF solution, but they could not be dissolved again without noticeable decomposition. This was a serious drawback for further investigations and in order to get more conventional precursors, we decided to use carbene adducts [7] of bis(tetramethylphospholyl)ytterbium; such kinds of

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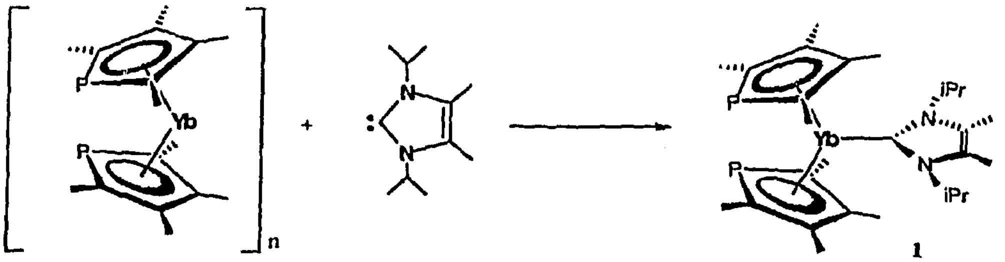


Fig 1

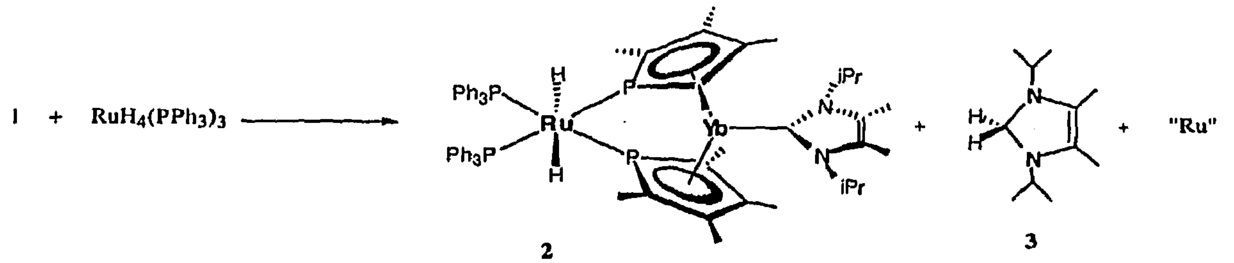


Fig 2

adducts were recently described [8] but their reactivity was not investigated. It could be of great interest to determine if the hydrogenolysis of the metal–carbone bond could provide an original pathway for the formation of the Ln–H bond.

Results and discussion

Synthesis of the adducts (tmp)$_2$Yb(carbene) **1a** *and* **1b**

The aromatic carbenes act as nucleophiles and are known to form adducts with electrophilic centers [8, 9]. When emerald-green, insoluble, THF free bis(tetramethylphospholyl)ytterbium: $[(tmp)_2Yb]_n$ [10], was added to a solution of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene [7a] (hereafter called ^{iPr}carbene) in toluene, it dissolves readily to give a brown solution. After concentration and cooling, analytically pure brown crystals of $(tmp)_2Yb(^{iPr}carbene)$ **1a** were obtained and isolated in 60% yield (fig 1).

1a is stable for weeks in toluene at room temperature. When a large excess amount of THF was added to a toluene solution of **1a**, the solution immediately turned red: THF removes the carbene from the adduct to give the known $(tmp)_2Yb(THF)_2$. The analogous complex **1b** $(tmp)_2Yb(^{Me}carbene)$ was obtained in a similar way from $[(tmp)_2Yb]_n$ and 1,3,4,5-tetramethylimidazol-2-ylidene [7a].

Formation of the bimetallic *$[(^{iPr}carbene)Yb(tmp)_2][RuH_2(PPh_3)_2]$* **2a**

A stoichiometric mixture of $(tmp)_2Yb(^{iPr}carbene)$ and $RuH_4(PPh_3)_2$ [5b] was dissolved in C_6D_6 and the reaction was monitored by NMR. After 30 minutes, both ^1H and ^{31}P spectra unambiguously showed the formation of the bimetallic **2a** species in ca 60% yield (fig 2). The liberation of free PPh_3 was observed and the signal of the four planar phosphorus atoms of **2a** appeared to be a AA′XX′ system. The reaction was not complete after this period. The NMR spectra were rather complicated because besides the signals of the bimetallic **2a** which was the major component, those of the remaining starting materials and of the hydrogenated carbene $C_2Me_2(N^iPr)_2CH_2$, **3a**, and numerous small signals were also present. The set of signals corresponding to **3a** were attributed by comparison with those of a pure sample prepared from the carbene in the following ways (fig 3):

- reaction with $RuH_4(PPh_3)_3$;

- successive addition of H^+ [from $HNEt_3BPh_4$] and of H^- (from $NaHBEt_3$).

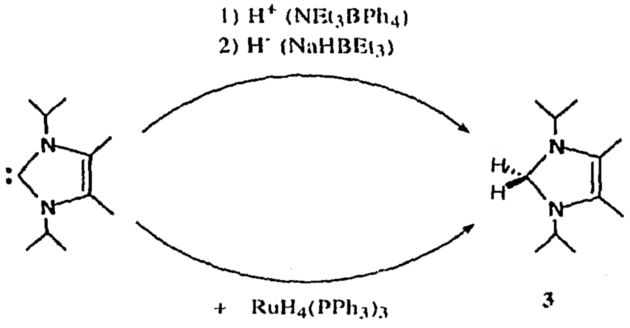
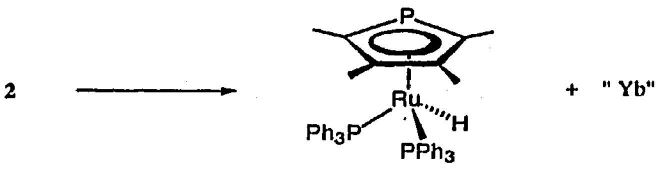


Fig 3

The protonation of an analogous carbene, 1,3-dimesitylimidazol-2-ylidene, was recently described [9c], but in these experiments the subsequent treatment of the salt by the basic NaH reagent instead of the nucleophilic $NaHBEt_3$, led to H_2 elimination and recovering of the starting material.

3a is extremely air sensitive and its mass spectrum could not be obtained. The presence of two hydrogen atoms on the C(2) carbon of the cycle is established from ^1H (integration) and ^{13}C NMR experiments.

The reaction between $(tmp)_2Yb(^{iPr}carbene)$ and $RuH_4(PPh_3)_2$ was complete after 24 hours at room temperature as judged by the disappearance of the signals of these materials; an important brown precipitate deposited, the bimetallic **2a** was still present, whereas the amounts of the hydrogenated carbene and of an 'impurity' significantly increased. This latter product was identified as the new compound $(tmp)RuH(PPh_3)_2$ **4**:



4

Fig 4

After 48 hours, the signals of **2a** disappeared completely and only the hydrogenated carbene **3a**, **4** and another compound: $(tmp)RuH(PPh_3)(^{iPr}carbene)$ **4'**, were present in the solution.

*Attempts to synthesize the bimetallic $[(^{Me}carbene)Yb(tmp)_2][RuH_2(PPh_3)_2]$ **2b***

The relatively low stability of the bimetallic **2a** was tentatively related to the steric hindrance due to the bulky isopropyl groups of the ^{iPr}carbene: strong nonbonding interactions between the methyl groups of the phospholyl and carbene ligands would push the former towards the ruthenium moiety and induce the ligand exchange leading to **4**. The synthesis of a less hindered complex, the ^{Me}carbene analogue **2b**, was undertaken from **1b** and $RuH_4(PPh_3)_3$; preliminary experiments were conducted on the NMR scale and unexpected results were obtained: gas (presumably H_2) evolution was observed and in the ^1H NMR spectrum, no trace of the hydrogenated carbene and no quintet hydridic signal. In the ^{31}P spectrum, no AA′ BB′ quartet was present, but in addition to the signal of the free PPh_3, a set of four new signals was observed. These NMR data, and especially the ^{31}P spectrum would imply that, if a bimetallic is formed (as suggested by the presence of free PPh_3), it would be a *cis* dihydride as precedently observed in uranium chemistry [6]. Due to the failure in the obtention of the expected complex, this reaction was not further investigated.

*Synthesis of $(tmp)RuH(PPh_3)_2$ **4** and proposed formula for **4'***

The new complex **4** was prepared in an analytically pure form by direct reaction of $RuHCl(PPh_3)_3$ and (tetramethylphospholyl)potassium (tmpK) [11] in toluene, isolated as a yellow solid. The formation of **4** was also observed after gentle heating (50 °C) during a few hours of the known ytterbium–ruthenium complex: $(PPh_3)_2RuH_2\text{-}\mu(tmp)_2Yb(THF)_2$ in benzene or toluene solution. It was also formed in an attempt to synthesize a bimetallic species from $RuHCl(PPh_3)_3$ and $(tmp)_2Yb(^{iPr}carbene)$. On the contrary, no formation of **4** was detected upon heating of the known $(PPh_3)_2RuH_2\text{-}\mu(tmp)_2MX_2$, where $MX_2 = ZrCl_2$, UCl_2 or $U(BH_4)_2$ [6]. These facts are in good agreement with the major covalent nature of the metal–ligand bonds in the zirconium or uranium complexes and with the more ionic character of this bond in lanthanide complexes.

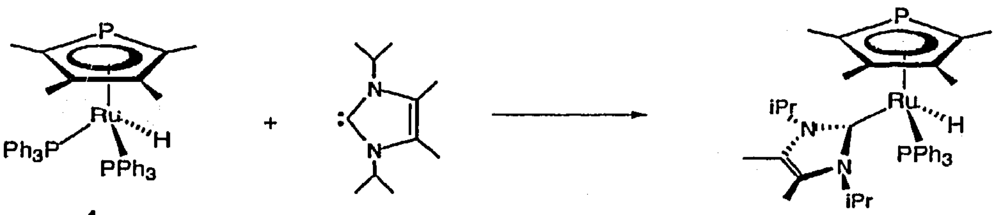
The proposed formula for **4'** was deduced from the multiplicity of the RuH signal which is a doublet and from the obtention of **4'** when **4** is heated in the presence of an excess of ^{iPr}carbene (fig 5). However, this reaction was slow and not complete (after 5 days the mixture contained 40% of unreacted **4**). Therefore it was not possible to isolate **4'** in this way.

Concluding remarks

Some interesting features emerge from these preliminary experiments:

It is confirmed that the stable nucleophilic carbenes can be used as very efficient hydrocarbon ligands to get soluble lanthanide derivatives.

The mechanism of the formation of **3a** is not obvious: **3a** is formed when **1a**, $RuH_4(PPh_3)_3$ and **2a** are together during the course of the reaction, or when **2a** is heated after the disappearance of $RuH_4(PPh_3)_3$. A partial dissociation of the carbene ligand in **1a** or **2a** in solution cannot be precluded, and then the reaction of this carbene with $RuH_4(PPh_3)_3$ (or with the RuH_2 moiety of **2a**) would lead to **3a** (by mixing



4 **4'**

Fig 5

together the ^{iPr}carbene and $RuH_4(PPh_3)_3$, **3a** is obtained). When **2a** is heated, ligand scrambling leading to **4** is facilitated, the unstable tmpYbH(carbene) remaining fragment would then rearrange into the stable **3a** and an insoluble Yb derivative. The hydrogen transfer onto the ^{iPr}carbene is not general because the formation of an analogous complex $C_2Me_2(NMe)_2CH_2$ **3b** did not occur during the reaction of the ^{Me}carbene with $RuH_4(PPh_3)_3$. In this case gas evolution could be observed, with the current liberation of PPh_3 and formation of a new ruthenium dihydrido complex (see Experimental section).

The obtention and stability of $HX(PPh_3)_2Ru$–$\mu(tmp)_2YbX'_n$ compounds is strongly dependent on the nature of both X and X′ ligands. When X = H and X′ = THF, a stable (in the solid state) bimetallic Ru–Yb is obtained; wher [illegible] ^{iPr}carbene, a transient bimetallic is formed in solution. When X′ = ^{Me}carbene, the formation of the trans dihydride bimetallic is not observed. To maintain the four phosphorous atoms in the same plan, the presence of bulky ligands on the Yb atom seems required. No formation of a stable bimetallic occurs when X = Cl, whereas the analogous Zr–Ru complex, $HClRu(tmp)_2ZrCl_2$, is stable.

The new complex $(tmp)RuH(PPH_3)_2$ is expected to be isostructural with the known $(C_5Me_5)RuH(PPh_3)_2$ [12]. Nevertheless, if both C_5Me_5 and tmp cycles are sterically equivalent, the latter acts as a much less electrodonating ligand and a comparative study of the reactivity of these two complexes is expected to evidence these electronic effects.

Experimental section

All solvents were thoroughly dried and purified by distillation over benzophenone ketyl under a nitrogen atmosphere. Deuterated NMR solvents (C_6D_6) were dried and degassed over a potassium–sodium alloy and distilled directly in the NMR tube.

Previously published methods were used for the synthesis of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (called ^{iPr}carbene) and of 1,3,4,5-tetramethylimidazol-2-ylidene (called ^{Me}carbene) [7], bis(tetramethylphospholyl)ytterbium: $(tmp)_2Yb$ [10] and (tetramethylphospholyl)potassium [11]. All synthetic procedures were performed under an atmosphere of dry oxygen-free nitrogen in a Jacomex glovebox or on a vacuum line.

NMR spectra were recorded on a Bruker AC 200 spectrometer. Proton NMR spectra were obtained at a frequency of 200.13 MHz. Samples prepared in benzene-d_6 were referenced to the broad singlet at δ 7.16 resulting from C_6D_5H. The ${}^{31}P$ NMR signals reported are referenced relative to external 85% aqueous H_3PO_4. All the ${}^{31}P$ spectra were performed with the broad band pulse (totally decoupled proton).

Analytical data were obtained on an EA1108 Fisons Apparatus in Dijon and from the Centre de Microanalyse of the CNRS at Gif/Yvette, France.

tmp_2Yb(carbene) ***1a*** *and* ***1b***

1a: Green and insoluble $Yb(tmp)_2$ [10] (150 mg, 0.33 mmol) was added to a toluene solution of ^{iPr}carbene [7] (60 mg, 0.33 mmol). The colorless solution was stirred at room temperature until the color became brown. After filtration and concentration, slow evaporation of toluene affords red brown crystals isolated in 60% yield (120 mg).

${}^1H$ NMR (benzene-d_6, ambient): δ (ppm) 1.22 (d, 12H, J = 6.92 Hz, *i*-Pr); 1.52 (s, 6H, Me); 2.10 (s, 12H, Meβ); 2.45 (m, 12H, J_{HP} = 10.4 Hz, Meα); 3.80 (hept, 2H, *i*-Pr).

${}^{31}P$ NMR (benzene-d_6, ambient): δ (ppm) 85 (s).

Anal calc from $C_{27}H_{44}N_2P_2Yb$: C, 51.34; H, 7.02; N, 4.43. Found: C, 51.41; H, 6.86; N, 4.27.

1b: In the same way, from $Yb(tmp)_2$ (135 mg, 0.29 mmol) and ^{Me}carbene [7] (40 mg, 0.32 mmol) 125 mg of brown crystals of **1b** were obtained (70% yield).

${}^1H$ NMR (benzene-d_6, ambient): δ (ppm) 3.00 (s, 6H, Me); 2.42 (d, 12H, J_{HP} = 9.76 Hz, Meα); 2.04 (s, 12H, Meβ); 1.33 (s, 6H, Me); 1.33.

${}^{31}P$ NMR (benzene-d_6, ambient): δ (ppm) 86 (s).

Anal calc from $C_{23}H_{36}N_2P_2Yb$: C, 48.0; H, 6.30; N, 4.87. Found: C, 47.44; H, 6.14; N, 4.03.

Formation of (^{iPr}carbene)Yb [$\mu(tmp)_2$]$RuH_2(PPh_3)_2$ ***2a***

In an NMR tube, tmp_2Yb(carbene) (10 mg, 0.016 mmol) and $RuH_4(PPh_3)_3$ [13] (14 mg, 0.016 mmol) were dissolved in 0.4 mL of C_6D_6. The NMR spectra of the brown solution, recorded immediately, shows the presence of the bimetallic complex:

${}^1H$ NMR: δ (ppm) −5.54 (qt, 2H, J_{HP} = 20.5 Hz, RuH); 0.87 (d, 12H, J = 5.9 Hz, *i*-Pr); 1.40 (s, 6H, Me); 1.78 (s, 12H, Meβ); 2.12 (m, 12H, J_{HP} = 14 Hz, Meα).

${}^{31}P$ NMR: δ (ppm) 66 (d, J_{PP} = 220 Hz, PPh_3); 96.4 (d, J_{PP} = 220 Hz, PC_4Me_4).

The solution contains also $C_2Me_2(N^iPr)_2CH_2$ (see below) and an unidentified ruthenium compound [${}^{31}P$ NMR: δ (ppm) 61 (s, 2P); 60 (d, 1P); 53 (d, 1P)]. After 24 h at room temperature, the starting materials were consumed; then, the signals of the bimetallic complex **2a** and those of the above-mentioned unknown complex decreased slowly whereas two new sets of signals, attributed (see below) to $tmpRuH(PPh_3)_2$ **4** (major component) and tmpRuH (PPh_3) (carbene) **4′** (minor), increased. After two days, only these two compounds and $C_2Me_2(N^iPr)_2CH_2$ were present in the tube.

Reaction of ***1b*** *with $RuH_4(PPh_3)_3$*

In an NMR tube, **1b** (9.5 mg, 0.016 mmol) and $RuH_4(PPh_3)_3$ [13] (15 mg, 0.016 mmol) were dissolved in 0.4 mL of benzene-d_6 at room temperature. After the dissolution of the solids, a gas evolution occurred, the NMR spectra showed the progressive disappearance of the starting materials and the growth of new signals. After 16 h at room temperature, the reaction was complete.

${}^1H$ NMR: δ (ppm), hydride signals: −6.53 (t, 20 Hz); −10.5 (m); −12.6 (m); −12.98 (m).

${}^{31}P$ NMR: δ (ppm) 84 (d, J_{PP} = 15 Hz, 1P); 71.1 (s, 1P); 65.8 (d, J_{PP} = 15 Hz, 1P); 46.8 (s, 1P); −7.1 (s, free PPh_3).

When similar experiments were conducted with an excess of $RuH_4(PPh_3)_3$ (3 or 4 equiv), the ${}^{31}P$ NMR spectrum was different: two (small) doublets were depicted: δ (ppm) 61.6 (d, 152 Hz), 31.3 (d, 152 Hz) near other signals: 65.0, 47.5 and −7.1 (free PPh_3).

$C_2Me_2(N^iPr)_2CH_2$ ***3a***

- *Method a*

In an NMR tube, carbene [7] (3 mg, 0.016 mmol) and $RuH_4(PPh_3)_3$ [13] (15 mg, 0.016 mmol) or $RuHCl(PPh_3)_3$

[14] under H_2 (15.4 mg, 0.016 mmol) were dissolved in 0.4 mL of benzene-d_6. After one day at room temperature, the NMR spectra showed the presence of **3**. The solvent was removed and pentane was added. The solution was filtered and evaporated to dryness. The white powder was analysed as **3a** by NMR in benzene-d_6.

- *Method b*

In an NMR tube, $HNEt_3BPh_4$ (9 mg, 0.02 mmol) was added to a C_6D_6 solution of carbene (4 mg, 0.02 mmol). After 2 h, the solution containing NEt_3 was eliminated, the precipitate dried and $NaHBEt_3$ (20 mL of a 1 M toluene solution, 0.02 mmol) was added with 0.4 mL of benzene-d_6. The spectra of the remaining solution revealed the presence of **3a**.

^1H NMR: δ (ppm) 0.97 (d, 12H, $J = 6.6$ Hz, iPr); 1.60 (s, 6H, Me); 3.32 (hept, 2H, $J = 6.6$ Hz, iPr); 4.20 (s, 2H, $C(2)H_2$).

^{13}C NMR: δ (ppm) 128.1 [C(4,5)], 61 [C(2)], 46.9 [N(1,3)-$\mathit{C}H(CH_3)_2$], 18.2 [N(1,3)-$CH(\mathit{C}H_3)_2$], 10.3 [C(4,5)-$\mathit{C}H_3$].

The ^{13}C NMR spectrum was recorded by the spinecho method: the C(2) carbon signal appears with reversed phase.

Reaction of $C_2Me_2(NMe)_2$ with $RuH_4(PPh_3)_3$

In an NMR tube, ^{Me}carbene, $C_2Me_2(NMe)_2$ [7] (ca 2.9 mg, 0.016 mmol) and $RuH_4(PPh_3)_3$ [13] (15 mg, 0.016 mmol) were dissolved in 0.4 mL of benzene-d_6. A strong gas evolution is observed.

^1H NMR, hydrides: δ (ppm) −6.56 (t, 1H, $J = 20$ Hz); −10.1 (t, 1H, $J = 29.5$ Hz).

^{31}P NMR: δ (ppm) 66.1 and 63.5 [Ru]PPh_3; −7.1, free PPh_3.

tmpRuH(PPh_3)$_2$ 4

- *Preliminary experiments*

In an NMR tube, 7 mg of (tetramethylphospholyl)potassium [11] and 20 mg of $RuHCl(PPh_3)_3$ [14] were mixed in 0.4 mL of deuteriated benzene and stirred by ultrasound. After 1 h, the purple crystals were consumed and **4** was formed in a nearly quantitative yield.

- *Synthesis*

A solution of (tetramethylphospholyl)potassium [11] (33 mg, 0.1 mmol) and $RuHCl(PPh_3)_3$ [14] (100 mg, 0.1 mmol) in toluene (15 mL) was stirred for 5 h at room temperature. The reddish-brown mixture was filtered and concentrated to 5 mL. Addition of pentane (5 mL) gave a trouble solution. After filtration, concentrating and cooling, yellow crystals of **4** analytically pure were isolated in 15% yield (15 mg).

^1H NMR: δ (ppm) −10.9 (t, 1H, $J = 32$ Hz, RuH); 1.37 (m, 12H, $J_{HP} = 10.7$ Hz, Meα); 1.58 (s, 12H, Meβ).

^{31}P NMR: δ (ppm) −34.9 (s, PC_4Me_4), 65 (s, PPh_3).

Anal calc for $C_{44}H_{43}P_3Ru$: C, 69.01; H, 5.66. Found: C, 68.96; H, 5.74.

tmpRuH(PPh_3)(carbene) 4′

In an NMR tube, (tmp)RuH$(PPh_3)_2$ **4** (10 mg, 0.013 mmol) and carbene in excess (2 equiv) were dissolved in THF/C_6D_6 (3:2). The solution was warmed at 70 °C during 4 days. The NMR spectra revealed the formation of **4′** (ratio of **4**/**4′** = 2:3).

^1H NMR: δ (ppm) −10 (d, 1H, $J = 50$ Hz, RuH).

^{31}P NMR: δ (ppm) −49.8 (s, PC_4Me_4); 66.6 (s, PPh_3).

Acknowledgments

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