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Lability of Ta-NHC adducts as a Synthetic Route Towards Heterobimetallic Ta/Rh Complexes

Ravi Srivastava,^a Elsje Alessandra Quadrelli^a and Clément Camp*^a

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We report the synthesis and characterization of a series of original tantalum/rhodium heterobimetallic species assembled by a bifunctional alkoxy-N-heterocyclic carbene (NHC) ligand platform (noted L). The heterotrimeric $[\text{Ta}(\text{CH}_2^t\text{Bu})(\text{CH}^t\text{Bu})(\mu\text{-L})\text{Rh}_2(\text{COD})_2\text{Cl}_2]_n$, **2**, and heterobimetallic $[\text{Ta}(\mu\text{-L})(\text{CH}^t\text{Bu})(\text{CH}_2^t\text{Bu})_2\text{Rh}(\text{COD})\text{Cl}]$, **4**, complexes are obtained upon treatment of $\text{Ta}(\text{L})(\text{CH}^t\text{Bu})(\text{CH}_2^t\text{Bu})_2$, **1**, with $[\text{Rh}(\text{COD})\text{Cl}]_2$. To avoid parasitic reactivity arising from the neopentylidene fragment in **1**, the peralkyl compound $\text{Ta}(\text{L})[\text{OSi}(\text{O}^t\text{Bu})_3](\text{CH}_2^t\text{Bu})_3$, **5**, resulting from the 1,2-addition of *tris*(tertbutoxysilanol) across the Ta=C alkylidene motif, is prepared. An unanticipated silanol-NHC adduct, $\{\text{HOSiO}^t\text{Bu}_3\}\{\text{Ta}(\text{L})[\text{OSi}(\text{O}^t\text{Bu})_3](\text{CH}_2^t\text{Bu})_3\}$, **6**, is formed when **1** is treated with two equivalents of $\text{HOSi}(\text{O}^t\text{Bu})_3$. Finally, treatment of **5** with $[\text{Rh}(\text{COD})\text{Cl}]_2$ provides the heterobimetallic complex $\{\text{Ta}(\mu\text{-L})[\text{OSi}(\text{O}^t\text{Bu})_3](\text{CH}_2^t\text{Bu})_3\text{Rh}(\text{COD})(\text{Cl})\}$, **7**, in high yield. This work highlights the reactivity of Ta-NHC adducts and the aptitude of the NHC motif to transfer from Ta to Rh which is used with profit as an efficient synthetic route to access early/late heterobimetallic complexes.

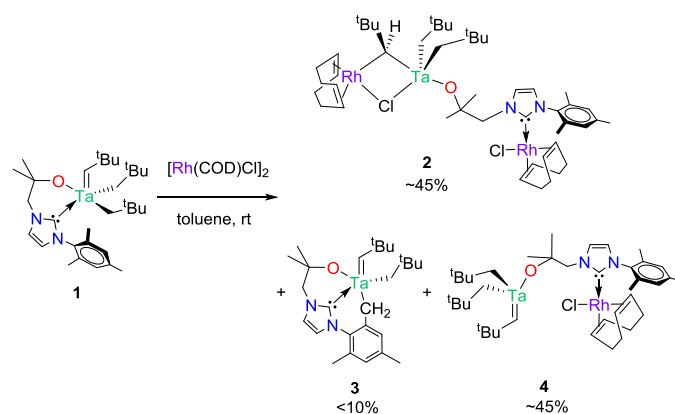
Introduction

Transmetalation is a key elementary reaction in organometallic chemistry which is frequently used for the preparation of organometallic derivatives^{1–3} and utilized with success in homogeneous catalysis, especially in cross-coupling reactions.^{4–6} Transmetalation approaches are well-established and popular for the synthesis of N-heterocyclic carbene (NHC) complexes because the direct metalation of NHC ligands often fails, due to the harsh basic conditions required for the deprotonation of imidazolium proligands which can lead to degradation. Silver(I) NHC derivatives have proven very successful for transmetalation purposes since they can be easily generated and are able to transfer the NHC moiety to a large diversity of metals.^{7–11} Cu(I)-NHC^{12–18} and W(O)-NHC^{19–22} synthons were also used as NHC transfer agents to provide less expensive and light-stable alternatives to their Ag congeners. However, besides group 10 and group 6 metal derivatives, little is known regarding the NHC transmetalation aptitude of other *d*-block NHC reagents to date.^{23–31} In our quest for a suitable ligand platform able to drive the assembly of early/late heterobimetallic species, we became interested in the coordination chemistry of a novel alkoxy-NHC ligand^{23,32} (noted L). Such bifunctional ligand, featuring two distinct coordination motifs, is particularly well poised for the stepwise construction of robust bimetallic assemblies, through the introduction of a late metal into a pre-formed alkoxy-NHC early metal complex. Surprisingly, despite the flagship role of NHC ligands in homogeneous catalysis, few early-late heterobimetallic species

based on NHCs have been isolated so far.^{23,33–35} As proof of principle, we have reported a preliminary study describing the encouraging insertion of $[\text{Rh}(\text{COD})\text{Cl}]_2$ into the Ta-NHC bond from $\text{Ta}(\text{N}^t\text{Bu})(\text{L})(\text{CH}_2^t\text{Bu})_2$.²³ Herein we report the generalization of the NHC transfer from Ta to Rh as an efficient synthetic route to access early/late heterobimetallic complexes.

Results and Discussion

The reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ with the tantalum-NHC complex **1**,²³ performed in toluene, yields a heteropolymetallic assembly of general formula $[\text{Ta}(\text{CH}_2^t\text{Bu})(\text{CH}^t\text{Bu})(\mu\text{-L})\text{Rh}_2(\text{COD})_2\text{Cl}_2]_n$, **2** (see below), along with two other co-products, **3** (in limited amounts) and **4** represented on Scheme 1. All attempts to separate **2** and **4** upon fractional crystallization of the crude mixture were unsuccessful. In particular, the heterometallic species **2** and **4** have similar solubilities and co-crystallized in the same reaction conditions.



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Scheme 1. Reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ with the tantalum-NHC complex **1** performed in toluene.

The cyclometallated complex **3** results from the thermal decomposition of **1**. Its structure was previously inferred on the basis of ^1H and ^{13}C NMR studies.²³ Here we report its solid-state structure (Figure 1), determined by single crystal X-ray crystallography, which provides evidence for the atom connectivity in **3**. The intramolecular C-H bond activation of an *ortho*-methyl group from the NHC mesityl substituent results in the formation of a C-C-O pincer-type ligand. The coordination geometry around the Ta cation is in between trigonal bipyramidal and square planar ($\tau_5 = 0.36$). The alkylidene moiety is clearly defined by the large Ta1-C21-C22 angle of $153.1(5)^\circ$ and the short Ta1=C21 bond ($1.922(6)$ Å). This bond length is significantly shorter than the other two Ta-C alkyl bonds lengths ($2.237(7)$ Å) and compares well with that of previously reported Ta(V) alkylidene complexes.^{23,36–40} The Ta-C_{NHC} bond distance (Ta1-C1 = $2.261(7)$ Å) is slightly shorter to that in found in **1** ($2.355(5)$ Å)²³ and falls in the range (2.22 – 2.40 Å) of the rare examples of tantalum NHC complexes reported to date.^{23,41–45} The Ta-C_{NHC} bond length is thus much longer than that of the Ta=C_{neopentylidene} which reflects the difference in the metal-carbene interactions (Fischer-type versus Schrock-type carbene).

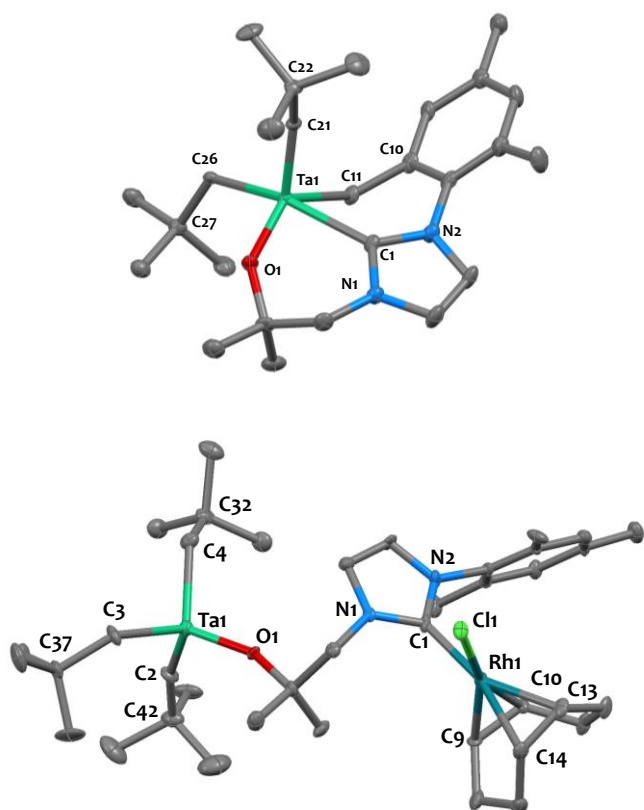
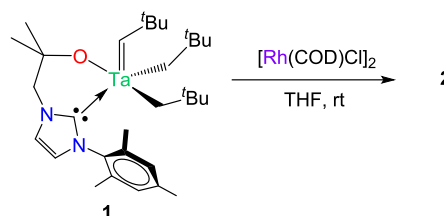


Figure 1. Solid-state molecular structure of **3** (top) and **4** (bottom) (30% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles ($^\circ$) for **3**: Ta1-O1 $1.892(5)$; Ta1-C1 $2.261(7)$; Ta1-C11 $2.237(7)$; Ta1-C21 $1.922(6)$; Ta1-C26 $2.237(7)$; N1-C1 $1.359(9)$; N2-C1 $1.362(9)$; O2-Ta1-C1 $80.8(2)$; N1-C1-N2 $103.1(6)$; Ta1-C11-C10 $115.8(5)$; Ta1-C21-C22 $153.1(5)$; Ta1-C26-C27 $124.4(4)$. For **4**: Ta1-O1 $1.837(7)$; Ta1-C2 $1.90(1)$; Ta1-C3 $2.14(1)$; Ta1-C4 $2.16(1)$; Rh1-C1 $2.04(1)$; Rh1-Cl1 $2.389(3)$; Rh1-C9 $2.08(1)$; Rh1-C10 $2.11(1)$; Rh1-C13 $2.18(1)$; Rh1-C14 $2.20(1)$; N1-C1

$1.38(1)$; N2-C1 $1.37(2)$; N1-C1-N2 $102.6(9)$; Ta1-C2-C42 $164(1)$; Ta1-C3-C37 $132.8(8)$; Ta1-C4-C32 $130.7(8)$.

Although the heterobimetallic complex $[\text{Ta}(\mu\text{-L})(\text{CH}^t\text{Bu})(\text{CH}_2^t\text{Bu})_2\text{Rh}(\text{COD})\text{Cl}]$, **4**, could not be isolated pure, its formation was clear on the basis of NMR data, which closely match that of the previously reported imido analogue, $[\text{Ta}(\mu\text{-L})(\text{N}^t\text{Bu})(\text{CH}_2^t\text{Bu})_2\text{Rh}(\text{COD})\text{Cl}]$.²³ In particular the ^1H NMR spectrum for **4** displays a singlet at $\delta = +3.93$ ppm attributed to the Ta neopentylene α -H. This signal correlates in the ^1H - ^{13}C HSQC NMR experiment to the characteristic neopentylidene ^{13}C resonance found at $\delta = +238.2$ ppm (singlet); this highly deshielded value is typical of Ta(V) alkylidenes.^{46–48} The ^{13}C resonance corresponding to the NHC carbene carbon appears as a doublet at $\delta = +184.5$ ppm ($^1J_{\text{Rh-C}} = 52$ Hz) which confirms Rh coordination to the NHC ligand.^{23,49} Furthermore, the solid-state structure of **4** was obtained by single crystal crystallography and is shown on Figure 1. The alkoxy-NHC ligand bridges the two metals: the “hard” alkoxy arm binds to Ta while the “soft” carbene ligand moiety is coordinated to Rh. The two metal centres are separated by $7.236(1)$ Å. The tantalum core adopts a pseudo-tetrahedral geometry ($\tau_4 = 0.95$) which is typical for 4-coordinate d^0 Ta(V) complexes.^{50,51} As expected, the Ta=C_{alkylidene} bond length ($1.90(1)$ Å) is significantly shorter than the Ta-C_{alkyl} distances ($2.14(1)$ and $2.156(1)$ Å), and falls in the expected range.^{23,36–40,52} The Rh centre adopts a square-planar coordination geometry ($\tau_4 = 0.09$) which is characteristic for 4-coordinate 16-valency electrons Rh(I) species. The Rh-carbene bond length ($2.040(1)$ Å) is comparable to that found in related Rh(I)-NHC species.^{23,49,53–56} As a result of the greater *trans* influence of the NHC donor, the Rh-COD distances *trans* to the carbene ($2.18(1)$ and $2.20(1)$ Å) are longer than those in the *cis* arrangement ($2.08(1)$ and $2.11(1)$ Å).



Scheme 2. Reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ with the tantalum-NHC complex **1** performed in THF.

Gratifyingly, when the same reaction is carried out in THF in place of toluene, the heteropolymetallic assembly **2** is obtained as sole product (Scheme 2). Optimization of the $1:[\text{Rh}(\text{COD})\text{Cl}]_2$ stoichiometric ratio (from 0.5:1 to 2:1) indicates that the nuclearity for **2** is $[\text{TaRh}_2]_n$, since **2** is also obtained along with unreacted starting materials when ratios lower or higher than 1:1 are used. This nuclearity is confirmed by high resolution mass spectrometry (m/z expected for $[\text{2-Cl}]^+$ 1107.3309 ; found 1107.3320 , see SI) as well as elemental analysis ($\text{mol}\% \text{Rh}:\text{mol}\% \text{Ta} = 1.9$), and the overall analysis is in excellent agreement with the proposed general formula for **2**.

The ^1H and ^{13}C NMR patterns for **2** are fairly complex, and denote the formation of an asymmetric species in solution. In particular, two sets of signals with close chemical shifts and integrating in a 1:1 ratio are observed, which indicate the formation of two independent components with slightly different environments. A proposed

structure for **2** is drawn on Scheme 1 on the basis of the NMR data. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **2** displays a characteristic signal at $\delta = +184.6$ ppm which corresponds to the NHC carbene carbon. This signal appears as a doublet ($^1J_{\text{Rh-C}} = 53.1$ Hz, Figure 2), which confirms the rhodium coordination to the NHC moieties in **2**. Two neopentylidene ^{13}C resonances (two doublets which overlap and appear as a pseudo-triplet, see Figure 2) are found at unusual chemical shifts ($\delta = +170.2$ and $+170.0$ ppm). These resonances are strongly high-field shifted compared to the corresponding signal in the starting complex **1** ($\delta = +250.4$ ppm)²³ and what classically found for Ta(V) alkylidenes.^{46–48} We attribute this result to rhodium coordination to the alkylidene carbons, which is confirmed by the coupling constant with rhodium ($^1J_{\text{Rh-C}} = 22.1$ Hz). This value is in close consonance with the $^1J_{\text{Rh-C}}$ values (20–23 Hz) observed for bridging methylene ligands in the related Ti-Rh heterobimetallic complexes $\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-X})\text{Rh}(\text{COD})$, ($\text{X} = \text{Cl}$, $o\text{-MeOC}_6\text{H}_4$, $p\text{-(CH}_3)_2\text{NC}_6\text{H}_4$).^{57,58} This characteristic signal evolves to a doublet of pseudo-triplets in the proton coupled ^{13}C NMR spectrum due to coupling with the neopentylidene $\alpha\text{-H}$ ($^1J_{\text{C-H}} = 116.7$ Hz, Figure 2) and correlates in the $^1\text{H}\text{-}^{13}\text{C}$ HSQC NMR experiment (Figure S6) to two characteristic neopentylidene $\alpha\text{-H}$ ^1H resonances found at $\delta = 4.78$ and 4.82 ppm. The remaining ^1H and ^{13}C resonances are typical and indicate an asymmetric compound, with, for instance, two pairs of diastereotopic doublets ($\delta = 4.50$, 4.55 , 6.12 and 6.16 ppm, $^2J_{\text{HH}} = 14.1$ Hz) for the N-CH_2 fragments of the two independent ligand components.

Unfortunately, all attempts to grow single crystals of **2** suitable for X-ray diffraction were unsuccessful. However, the spectroscopic data support the formation of a bridging alkylidene moiety connecting the early and the late metal, as proposed on Scheme 1. Heterobimetallic systems constructed around a bridging alkylidene motif are rare, despite their particular interest for reactivity purposes.^{59–64}

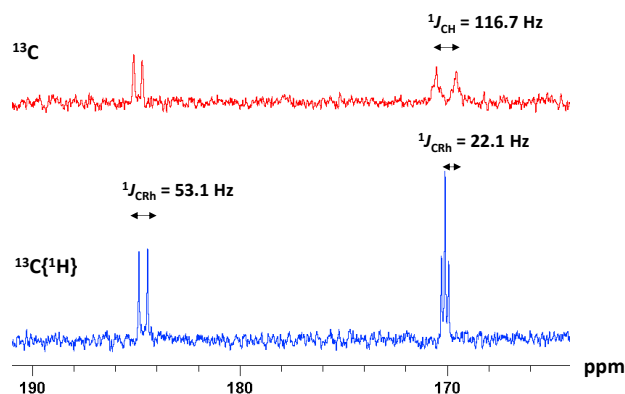
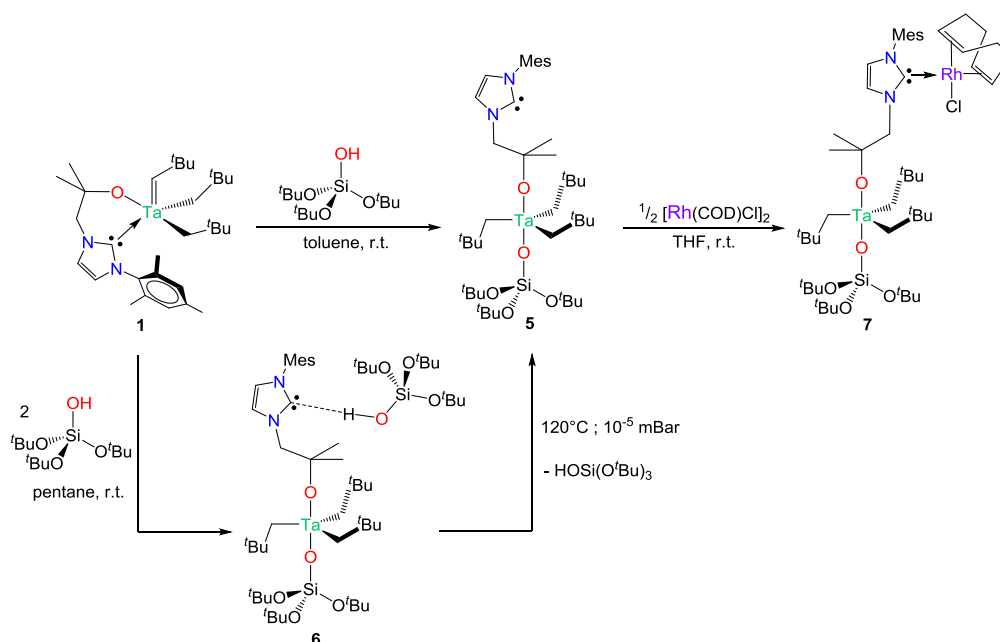


Figure 2. ^{13}C NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2** showing characteristic signals at $\delta = +184.6$, $+170.2$ and $+170.0$ ppm demonstrating transmetallation and rhodium coordination to both the NHC and the alkylidene ligands.

From this first set of experiments we can draw two main conclusions: 1) the NHC-Ta adduct is labile and NHC transmetallation from Ta to Rh occurs readily; 2) the neopentylidene fragment in **1** is highly reactive, and presumably reacts both with $[\text{Rh}(\text{COD})\text{Cl}]_2$ to yield species of higher nuclearity, and with the ligand's mesityl group to form a cyclometallated species. This hampers clean formation of a heterobimetallic species through simple Ta to Rh NHC transmetallation from **1**.

In order to overcome this limitation, we prepared a more stable Ta-siloxy derivative since siloxides are known to be excellent ligands for stabilizing oxophilic metal species.^{48,65–71} Treatment of **1** with 1 equivalent of tris(*tert*butoxy)silanol cleanly yields complex **5** resulting from the formal 1,2-addition of the silanol hydroxyl group across the $\text{Ta}=\text{C}$ alkylidene motif (Scheme 3). Unlike **1**, compound **5** features good thermal stability (up to 110°C) and was fully characterized through ^1H , ^{13}C NMR and IR spectroscopy and elemental analysis.



Scheme 3. Synthesis of complexes **5**, **6** and **7**.

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The ^1H NMR and the ^{13}C NMR spectra of complex **5** in C_6D_6 does not contain signals corresponding to alkylidene proton/carbon of a putative $\text{Ta}=\text{CH}(\text{tBu})$ motif which is in accordance with a formal 1,2-addition of the silanol hydroxyl onto the tantalum neopentylidene fragment. The ^{13}C NMR spectrum of **5** displays a characteristic signal at $\delta = +219.4$ ppm corresponding to the carbenic carbon of the NHC ligand. Such a downfield shift of this signal (as compared to corresponding $\delta(^{13}\text{C}_{\text{NHC}}) = 203.1$ and 205.2 ppm in complexes **1** and **3** respectively)²³ is evocative of free carbenes which are not interacting with transition metal centres (typical range: 210–220 ppm).^{72,73} Accordingly, the NHC moiety in **5** most likely do not interact with the Ta in **5**, as represented on Scheme 3, which is also in agreement with the reactivity of **1** (see below).

Interestingly, we discovered that addition of two equivalents of $\text{HOSi}(\text{O}^t\text{Bu})_3$ onto **1** affords an unanticipated silanol-NHC adduct, $\{\text{HOSi}(\text{O}^t\text{Bu})_3\}\{\text{Ta}(\text{L})[\text{OSi}(\text{O}^t\text{Bu})_3](\text{CH}_2^t\text{Bu})_3\}$, **6** (Scheme 4 and SI). The formation of **6** corroborates that the NHC moiety in **5** is available for further reactivity. This behavior is somewhat unexpected since further treatment of Ta-alkyl derivatives with silanols usually leads to protonolysis and formation of Ta siloxides with release of alkane.^{74,75} Here the NHC-silanol adduct formation quenches the protonolysis reactivity. Quite remarkably, thermal treatment (120°C) of **6** under vacuum (10^{-5} mBar) does not trigger protonolysis of a Ta-neopentyl moiety observed in related systems.⁵² Instead, the free NHC species **5** is quantitatively restored, through sublimation of the H-bonded ancillary $\text{HOSi}(\text{O}^t\text{Bu})_3$ molecule (Figure S11).

The availability of the carbenic carbon in complex **5** is exploited in the metallation reaction with rhodium. Complex **5** was treated with 0.5 equivalents of $[\text{Rh}(\text{COD})\text{Cl}]_2$ in THF at room temperature to selectively afford the desired heterobimetallic complex $\{\text{Ta}(\mu\text{-L})[\text{OSi}(\text{O}^t\text{Bu})_3](\text{CH}_2^t\text{Bu})_3\}\text{Rh}(\text{COD})(\text{Cl})$, **7**, in high yield (Scheme 3). The rhodium coordination to the NHC moiety in solution is confirmed by the ^{13}C NMR spectrum of complex **7** in C_6D_6 which displays a characteristic resonance at $\delta = +184$ ppm, strongly shifted downfield compared to **5** as expected, with a $^1J_{\text{Rh-C}}$ coupling constant of 52 Hz which is distinctive of a $\text{Rh-C}_{\text{carbene}}$ interaction. The coordination of COD to rhodium is confirmed by the ^1H NMR spectrum of complex **7** which shows characteristic signals at $\delta = 2.46, 2.87, 4.70$ and 4.92 ppm corresponding to the Rh-bound sp^2 protons of the cyclooctadiene ligand. As a result of Rh coordination, the alkoxy-NHC ligand backbone adopts a more rigid conformation, which is reflected notably by the N-CH_2 ^1H NMR signal (singlet integrating for 2H at $\delta = 4.80$ ppm in **5**) which splits into two doublets at $\delta = 4.34$ and 6.12 ppm ($^2J_{\text{HH}} = 14.0$ Hz) in **7**.

Finally the formula of **7** is supported by elemental analysis and its solid-state structure, determined by X-ray crystallography. A view of the structure is reproduced on Figure 3 and confirms that Rh is coordinated to the NHC moiety. As in **6**, the tantalum atom adopts a

trigonal bipyramid coordination geometry ($\tau_5 = 0.95$) with the neopentyl ligands in equatorial position and the two oxygen donors in apical position. The Ta-C and Ta-O bond distances are as expected.^{23,74} The rhodium centre adopts a pseudo square-planar geometry ($\tau_4 = 0.06$), which is characteristic of d^8 Rh(I) species. The NHC ring is tilted with respect to the pseudo-D_{4h} plane (dihedral angle $68.1(2)^\circ$), and the Rh-C_{NHC} bond distance ($2.033(7)$ Å) is in the range of reported values for related Rh-NHC complexes.^{23,49,53–56} The Rh-C_{COD} bond distances in trans position with respect to the NHC ligand ($2.162(8)$ and $2.182(8)$ Å) are slightly elongated compared to that trans to the chloride ($2.090(8)$ and $2.101(7)$ Å), which is in agreement with the strong sigma donation of the NHC. Both metals lie far away from one another and are separated by $6.6997(8)$ Å.

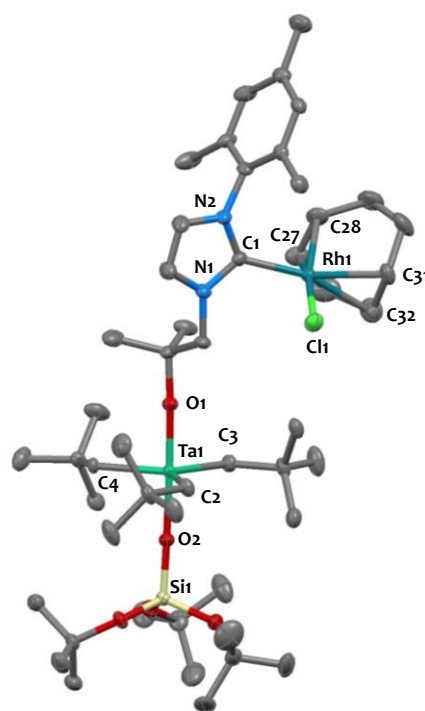


Figure 3. Solid-state molecular structure of **7** (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Ta1-O1 1.882(4); Ta1-O2 1.912(4); Ta1-C2 2.165(6); Ta1-C3 2.184(6); Ta1-C4 2.163(7); Rh1-C1 2.033(7); Rh1-C11 2.374(2); Rh1-C27 2.090(8); Rh1-C28 2.101(7); Rh1-C31 2.162(8); Rh1-C32 2.182(8); N1-C1 1.364(8); N2-C1 1.362(8); O1-Ta1-O2 178.2(2); N1-C1-N2 102.7(6); C1-Rh1-Cl1 85.5(2).

Conclusions

In summary we have described the synthesis and characterization of a series of original tantalum/rhodium

heterobimetallic species assembled by a bifunctional alkoxy-NHC ligand platform. We have evidenced the reactivity of the Ta-NHC motif and its aptitude to accommodate a rhodium centre. More generally, this study raises the question of ligand lability and coordination strength in metal-NHC complexes: NHCs are not necessarily strongly bound ancillary ligands, as often regarded, but can exchange between different metal ions. This work also highlights the utility of this alkoxy-NHC ligand to support heterobimetallic assemblies. Future studies will be devoted to the generalization of this synthetic strategy to various metal-metal couples and investigate the reactivity of the resulting heterobimetallic species.

Experimental Section

General considerations.

Unless otherwise noted, all reactions were performed either using standard Schlenk line techniques or in an MBraun inert atmosphere glovebox under an atmosphere of purified argon (<1 ppm O₂/H₂O). Glassware and cannulae were stored in an oven at ~100 °C for at least 12 h prior to use. Toluene, *n*-pentane and THF were purified by passage through a column of activated alumina, dried over Na/benzophenone, vacuum-transferred to a storage flask and freeze-pump-thaw degassed prior to use. THF-*d*₈ and C₆D₆ were dried over Na/benzophenone vacuum-transferred to a storage flask and freeze-pump-thaw degassed prior to use. Complex **1** was prepared according to the literature procedure.²³ All other reagents were acquired from commercial sources and used as received. NMR spectra were recorded on Bruker AV-300, AVQ-400 and AV-500 spectrometers. Chemical shifts were measured relative to residual solvent peaks, which were assigned relative to an external TMS standard set at 0.00 ppm. ¹H and ¹³C NMR assignments were routinely confirmed by ¹H–¹H COSY and ¹H–¹³C HSQC and HMBC experiments. Samples for IR spectroscopy were prepared in a glovebox, sealed under argon in a DRIFT cell equipped with KBr windows and analysed on a Nicolet 6700 FT-IR spectrometer. Elemental analyses were performed either at the School of Human Sciences, Science Centre, London Metropolitan University or at Mikroanalytisches Labor Pascher, Germany. The X-ray structural determinations were performed at the Centre de Diffractométrie Henri Longchambon, UCBL, Villeurbanne. Details concerning X-ray diffraction analyses are provided in the supporting information. CCDC 1980990–1980993 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Synthetic procedures.

Synthesis of 2. A 4 mL yellow THF solution of [Rh(COD)Cl]₂ (95 mg, 0.19 mmol, 1.0 equiv) was added dropwise to an orange stirring solution of complex Ta(L)(CH^tBu)(CH₂^tBu) **1** (125 mg, 0.19 mmol, 1.0 equiv) in 6 ml of THF. The reaction mixture was stirred at room temperature for 4h, and then the volatiles were evaporated to dryness. The resulting yellow powder was solubilized in THF, layered with pentane and stored at -40°C for

1 week to yield **2** as a yellow microcrystalline solid (175 mg, 0.15 mmol, 79% yield). ¹H NMR (500 MHz, C₆D₆, 296K) δ = 1.45 (s, 9H, CH₂^tBu), 1.47 (s, 9H, CH₂^tBu), 1.47 (s, 9H, CH^tBu), 1.49 (s, 9H, CH^tBu), 1.55 (s, 9H, CH^tBu), 1.58 (s, 9H, CH^tBu), 1.64 (s, 6H, CH₃), 1.65 (s, 6H, CH₃), 1.65 (s, 3H, *p*-CH₃Mes), 1.66 (s, 3H, *p*-CH₃Mes), 1.81 (d, 1H, TaCH₂), 1.82 (s, 3H, CH₃), 1.84 (s, 3H, CH₃), 1.85 (d, 1H, TaCH₂), 1.86 (d, 1H, TaCH₂), 1.87 (d, 1H, TaCH₂), 1.88 (br m, 2H, COD), 1.90 (d, 1H, TaCH₂), 1.91 (d, 1H, TaCH₂), 1.97 (br m, 6H, COD), 2.07 (br m, 4H, COD), 2.15 (s, 6H, *o*-CH₃Mes), 2.21 (br m, 2H, COD), 2.37 (br m, 2H, COD), 2.45 (br m, 2H, COD), 2.69 (s, 3H, *o*-CH₃Mes), 2.70 (s, 3H, *o*-CH₃Mes), 2.71 (br m, 2H, COD), 3.08 (m, 2H, COD), 3.14 (d, ²J_{HH} = 9.7 Hz, 1H, TaCH₂), 3.14 (d, ²J_{HH} = 9.7 Hz, 1H, TaCH₂), 3.59 (m, 2H, COD), 3.81 (m, 2H, COD), 3.90 (m, 2H, COD), 4.50 (d, ²J_{HH} = 13.7 Hz, 1H, NCH₂), 4.55 (d, ²J_{HH} = 13.7 Hz, 1H, NCH₂), 4.78 (s, 1H, Ta=CH^tBu), 4.82 (s, 1H, Ta=CH^tBu), 5.12 (m, 2H, COD), 5.30 (m, 4H, COD), 5.38 (m, 2H, COD), 5.93 (d, ³J_{HH} = 1.7 Hz, 1H, CH_{imid}), 5.94 (d, ³J_{HH} = 1.7 Hz, 1H, CH_{imid}), 6.12 (d, ²J_{HH} = 13.7 Hz, 1H, NCH₂), 6.16 (d, ²J_{HH} = 13.7 Hz, 1H, NCH₂), 6.62 (d, ³J_{HH} = 1.7 Hz, 1H, CH_{imid}), 6.68 (s, 2H, *m*-CH₃Mes), 6.89 (s, 2H, *m*-CH₃Mes). ¹³C{¹H} NMR (125.7 MHz, C₆D₆, 296K) δ = 17.6 (*p*-CH₃Mes), 17.7 (*p*-CH₃Mes), 20.4 (*o*-CH₃Mes), 21.1 (*o*-CH₃Mes), 27.7 (*o*-CH₃Mes), 28.2 (*o*-CH₃Mes), 28.2 (CH₂COD), 28.5 (CH₂COD), 28.8 (CH₂COD), 29.1 (CH₂COD), 29.3 (CH₂COD), 29.4 (CH₂COD), 29.6 (CH₂COD), 29.7 (CH₂COD), 29.8 (CH₃), 29.8 (CH₃), 31.8 (CH₃), 31.9 (CH₃), 34.6 (CH₂COD), 34.8 (CH₂COD), 34.9 (CH₂COD), 35.0 (CH₂COD), 35.5 (^tBu), 35.9 (^tBu), 36.0 (^tBu), 36.0 (^tBu), 36.2 (^tBu), 37.0 (^tBu), 37.4 (^tBu), 37.5 (^tBu), 43.6 (^tBu), 43.8 (^tBu), 62.35 (NCH₂), 62.4 (NCH₂), 68.6 (m, 4 CH_{COD}), 69.4 (d, ¹J_{Rh-C} = 15 Hz, CH_{COD}), 69.6 (d, ¹J_{Rh-C} = 15 Hz, CH_{COD}), 75.8 (d, ¹J_{Rh-C} = 18 Hz, CH_{COD}), 76.4 (d, ¹J_{Rh-C} = 18 Hz, CH_{COD}), 85.9 (OC), 86.0 (OC), 92.3 (Ta-CH₂), 92.5 (Ta-CH₂), 96.3 (d, ¹J_{Rh-C} = 6 Hz, CH_{COD}), 96.5 (d, ¹J_{Rh-C} = 6 Hz, CH_{COD}), 97.2 (d, ¹J_{Rh-C} = 6 Hz, CH_{COD}), 97.3 (d, ¹J_{Rh-C} = 6 Hz, CH_{COD}), 97.4 (d, ¹J_{Rh-C} = 6 Hz, CH_{COD}), 97.5 (d, ¹J_{Rh-C} = 6 Hz, CH_{COD}), 97.7 (d, ¹J_{Rh-C} = 6 Hz, CH_{COD}), 97.8 (d, ¹J_{Rh-C} = 6 Hz, CH_{COD}), 105.4 (Ta-CH₂), 105.6 (Ta-CH₂), 122.7 (CH_{imid}), 122.7 (CH_{imid}), 122.8 (CH_{imid}), 122.8 (CH_{imid}), 130.0 (CH_{Ar}), 134.5 (C_{Ar}), 134.6 (C_{Ar}), 137.1 (C_{Ar}), 138.0 (C_{Ar}), 138.9 (C_{Ar}), 170.0 (d, ¹J_{Rh-C} = 22 Hz, Ta=C), 170.2 (d, ¹J_{Rh-C} = 22 Hz, Ta=C), 184.6 (d, ¹J_{Rh-C} = 53 Hz, Rh-C_{carbene}). Anal. calcd for C₄₇H₇₇N₂OCl₂Rh₂Ta: C, 49.35; H, 6.79; N, 2.45; Cl, 6.20, Rh, 17.9; Ta, 15.8. Found: C, 49.46; H, 6.80; N, 2.51; Cl, 6.03, Rh, 17.5; Ta, 15.8.

Reaction of 1 with [Rh(COD)Cl]₂ in toluene. A 6 mL yellow toluene solution of [Rh(COD)Cl]₂ (151 mg, 0.31 mmol, 0.5 equiv) was added dropwise to an orange stirring solution of complex Ta(L)(CH^tBu)(CH₂^tBu) **1** (400 mg, 0.6 mmol, 1.0 equiv) in 6 ml of toluene. The reaction mixture was stirred at room temperature for 4h, yielding a brown solution which was evaporated to dryness. Analysis of the crude reaction mixture by ¹H NMR reveals the formation of a mixture of species containing **2**, **3** and **4**. Fractional recrystallization of the solid residue from saturated pentane solutions at -40°C yielded a solid containing a mixture of **2** and **4**. Unfortunately, all attempts to further separate these species were unsuccessful since feature similar solubilities and co-crystallize in the same conditions. Single crystals of **3** and **4** were grown from saturated pentane solutions of the crude mixture stored at -40°C. NMR data for **4**: ¹H NMR (500 MHz,

C_6D_6 , 296K) $\delta = 0.51$ (d, $^3J_{HH} = 13.3$ Hz, 1H, TaCH₂), 0.61 (d, $^3J_{HH} = 13.3$ Hz, 1H, TaCH₂), 1.20 (s, 9H, CH₂^tBu), 1.21 (s, 9H, CH₂^tBu), 1.33 (s, 9H, CH^tBu), 1.37 (d, $^3J_{HH} = 13.3$ Hz, 1H, TaCH₂), 1.42 (d, $^3J_{HH} = 13.3$ Hz, 1H, TaCH₂), 1.51 (br m, 2H, COD), 1.57 (s, 6H, CH₃), 1.69 (br m, 2H, COD), 1.71 (s, 3H, *p*-CH₃Mes), 1.80 (br m, 1H, COD), 1.98 (br m, 1H, COD), 2.11 (br m, 1H, COD), 2.16 (s, 3H, *o*-CH₃Mes), 2.28 (br m, 1H, COD), 2.69 (s, 3H, *o*-CH₃Mes), 3.19 (m, 1H, COD), 3.51 (m, 1H, COD), 3.93 (s, 1H, Ta=CH^tBu), 4.65 (d, $^2J_{HH} = 14.3$ Hz, 1H, NCH₂), 5.31 (m, 1H, COD), 5.41 (m, 1H, COD), 5.78 (d, $^2J_{HH} = 14.3$ Hz, 1H, NCH₂), 6.00 (d, $^3J_{HH} = 1.9$ Hz, 1H, CH_{imid}), 6.68 (s, 1H, *m*-CH_{Mes}), 6.89 (s, 1H, *m*-CH_{Mes}), 7.29 (d, $^3J_{HH} = 1.9$ Hz, 1H, CH_{imid}). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6 , 296K) $\delta = 17.8$ (*p*-CH₃Mes), 20.3 (*o*-CH₃Mes), 28.4 (*o*-CH₃Mes), 28.9 (CH₂COD), 29.2 (CH₂COD), 30.1 (CH₃), 30.9 (CH₃), 32.5 (CH₂COD), 34.1 (^tBu), 34.3 (CH₂COD), 34.8 (^tBu), 34.9 (^tBu), 35.0 (^tBu), 46.2 (^tBu), 62.5 (NCH₂), 68.0 (d, $^1J_{Rh-C} = 14$ Hz, CH_{COD}), 85.3 (OC), 94.8 (Ta-CH₂^tBu), 95.1 (Ta-CH₂^tBu), 97.1 (d, $^1J_{Rh-C} = 14$ Hz, CH_{COD}), 122.3 (CH_{imid}), 122.9 (CH_{imid}), 128.6 (CH_{Ar}), 130.1 (CH_{Ar}), 134.5 (C_{Ar}), 137.0 (C_{Ar}), 138.0 (C_{Ar}), 138.8 (C_{Ar}), 184.5 (d, $^1J_{Rh-C} = 52$ Hz, Rh-C_{carbene}), 238.2 (s, Ta=C).

Synthesis of 5. A 4 mL colorless toluene solution of tris(tert-butoxy) silanol (54 mg, 0.21 mmol, 1.0 equiv) was added dropwise to an orange stirring solution of complex Ta(L)(CH^tBu)(CH₂^tBu) **1** (135 mg, 0.21 mmol, 1.0 equiv) in 6 mL of toluene. The color of the solution turned light cream instantaneously. The reaction mixture was stirred at room temperature for 3h, and then the volatiles evaporated to dryness to yield complex **5** (167 mg, 0.18 mmol, 87% yield). 1H NMR (400 MHz, C_6D_6 , 296K) $\delta = 1.34$ (s, 27H, CH₂^tBu), 1.50 (s, 27H, O^tBu), 1.53 (s, 6H, Ta-CH₂), 1.84 (s, 6H, CH₃), 2.11 (s, 6H, *o*-CH₃Mes), 2.16 (s, 3H, *p*-CH₃Mes), 4.80 (s, 2H, NCH₂), 6.39 (d, $^3J_{HH} = 1.5$ Hz, 1H, CH_{imid}), 6.66 (d, $^3J_{HH} = 1.5$ Hz, 1H, CH_{imid}), 6.81 (s, 2H, *m*-CH_{Mes}). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6 , 296K) $\delta = 18.1$ (*o*-CH₃Mes), 21.0 (*p*-CH₃Mes), 27.3 (CH₃), 32.4 (Ta-CH₂C(CH₃)₃), 34.6 (Ta-CH₂C(CH₃)₃), 35.9 (SiOC(CH₃)₃), 61.4 (NCH₂), 73.4 (SiOC(CH₃)₃), 84.8 (OC(CH₃)₂(CH₂N)), 90.4 (Ta-CH₂^tBu), 120.2 (CH_{imid}), 120.7 (CH_{imid}), 127.9 (CH_{Ar}), 128.0 (CH_{Ar}), 129.1 (C_{Ar}), 135.5 (C_{Ar}), 137.0 (C_{Ar}), 139.3 (C_{Ar}), 219.5 (s, C_{NHC}). DRIFT (25°C, KBr solid solution under argon) 2972.6 (s, ν_{C-H}), 2955.0 (s, ν_{C-H}), 2897.7 (m, ν_{C-H}), 2859.4 (m, ν_{C-H}), 1495.2 (w), 1469.5 (m), 1391.0 (m), 1364.4 (s), 1241.0 (s), 1215.5 (m), 1190.0 (m), 1158.3 (m), 1079.4 (m), 1066.5 (s), 1031.3 (m), 976.2 (m), 945.1 (s), 854.1 (w), 828.3 (w), 799.1 (m), 713.1 (m), 695.1 (m), 583.8 (w), 570.4 (w). Anal. calcd for C₄₃H₈₁N₂O₅SiTa: C, 56.44; H, 8.92; N, 3.06. Found: C, 56.29; H, 9.02; N, 3.05.

Synthesis of 6. A 4 mL colorless pentane solution of tris(tert-butoxy) silanol (243 mg, 0.92 mmol, 2.0 equiv) was added dropwise to an orange stirring solution of complex Ta(L)(CH^tBu)(CH₂^tBu) **1** (300 mg, 0.46 mmol, 1.0 equiv) in 16 mL of pentane. The color of the reaction turned gradually from yellow to pale cream. The reaction mixture was stirred at room temperature for 3h, and then the volatiles evaporated to dryness. The solid residue was extracted with 10 mL pentane, filtered and stored at -40°C for 2 days to yield adduct **6** as a white crystalline solid (448 mg, 0.38 mmol, 83% yield). Single

crystals of **6** suitable for X-ray diffractions were grown from a saturated THF solution at -40°C. 1H NMR (500 MHz, C_6D_6 , 296K) $\delta = 1.34$ (s, 27H, CH₂^tBu), 1.44 (s, 27H, O^tBu), 1.50 (s, 27H, O^tBu), 1.52 (s, 6H, Ta-CH₂), 1.85 (s, 6H, CH₃), 2.10 (s, 6H, *o*-CH₃Mes), 2.18 (s, 3H, *p*-CH₃Mes), 4.77 (s, 2H, NCH₂), 6.25 (s, 1H, CH_{imid}), 6.67 (s, 1H, CH_{imid}), 6.82 (s, 2H, *m*-CH_{Mes}), 7.78 (s, 1H, SiOH). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6 , 296K) $\delta = 18.1$ (*o*-CH₃Mes), 21.0 (*p*-CH₃Mes), 27.5 (CH₃), 31.9 (SiOC(CH₃)₃), 32.4 (Ta-CH₂C(CH₃)₃), 34.6 (Ta-CH₂C(CH₃)₃), 35.9 (SiOC(CH₃)₃), 61.0 (NCH₂), 71.9 (SiOC(CH₃)₃), 73.4 (SiOC(CH₃)₃), 84.8 (OC(CH₃)₂(CH₂N)), 90.2 (Ta-CH₂^tBu), 120.3 (CH_{imid}), 121.5 (CH_{imid}), 129.2 (CH_{Ar}), 135.3 (C_{Ar}), 137.8 (C_{Ar}), 138.1 (C_{Ar}), 206.8 (s, C_{NHC}). DRIFT (25°C, KBr solid solution under argon) 3164.7 (w, ν_{C-H}), 3130.3 (w, ν_{C-H}), 2972.6 (s, ν_{C-H}), 2953.1 (s, ν_{C-H}), 2898.0 (m, ν_{C-H}), 2858.9 (m, ν_{C-H}), 1468.3 (m), 1385.4 (m), 1364.1 (s), 1239.3 (s), 1221.3 (m), 1192.3 (s), 1160.8 (m), 1061.6 (s), 1026.9 (m), 975.1 (m), 954.8 (s), 934.6 (m), 848.6 (w), 825.3 (m), 797.9 (w), 747.2 (m), 695.5 (m), 627.1 (w), 571.5 (m). Anal. calcd for C₅₅H₁₀₉N₂O₉Si₂Ta: C, 56.00; H, 9.31; N, 2.37. Found: C, 55.99; H, 9.34; N, 2.35.

Synthesis of 7. An orange THF solution (6 mL) of the [Rh(COD)Cl]₂ dimer (108.4 mg, 0.22 mmol, 0.5 equivalent) was added dropwise to the creamy THF solution (6 mL) of complex **5** (354 mg, 0.38 mmol, 1.0 equivalent) at room temperature. The reaction mixture was stirred for 14 hr at room temperature and then the volatiles were removed under vacuum to yield a yellow powder. The solid was dissolved in 4 mL THF and then let to crystallize at -40°C to yield **6** as yellow microcrystalline solid (486 mg, 0.38 mmol, 85% yield). Single crystals suitable for X-ray diffraction were grown in a similar fashion. 1H NMR (500 MHz, THF-*d*₈, 296K) $\delta = 1.25$ (s, 27H, CH₂C(CH₃)₃), 1.30 (br m, 2H, COD), 1.40 (s, 6H, TaCH₂), 1.47 (s, 27H, O^tBu), 1.51 (br m, 1H, COD), 1.79 (br m, 2H, COD), 1.84 (s, 3H, CH₃), 1.86 (s, 3H, CH₃), 1.89 (br m, 1H, COD), 1.94 (s, 3H, *p*-CH₃Mes), 2.09 (br m, 2H, COD), 2.37 (s, 3H, *o*-CH₃Mes), 2.46 (m, 1H, COD), 2.53 (s, 3H, *o*-CH₃Mes), 2.87 (m, 1H, COD), 4.34 (d, $^2J_{HH} = 14.0$ Hz, 1H, NCH₂), 4.70 (m, 1H, COD), 4.92 (m, 1H, COD), 6.12 (d, $^2J_{HH} = 14.0$ Hz, 1H, NCH₂), 6.96 (s, 1H, CH_{Mes}), 7.07 (d, $^3J_{HH} = 1.8$ Hz, 1H, CH_{imid}), 7.15 (s, 1H, CH_{Mes}), 7.37 (d, $^3J_{HH} = 1.8$ Hz, 1H, CH_{imid}). $^{13}C\{^1H\}$ NMR (125.7 MHz, THF-*d*₈, 296K) $\delta = 17.6$ (*p*-CH₃Mes), 20.2 (*o*-CH₃Mes), 20.9 (*o*-CH₃Mes), 25.7 (CH₂COD), 27.5 (CH₂COD), 27.9 (CH₃), 28.0 (CH₃), 30.5 (CH₂COD), 31.3 (CH₂COD), 32.5 (Ta-CH₂C(CH₃)₃), 35.3 (Ta-CH₂C(CH₃)₃), 36.1 (SiOC(CH₃)₃), 62.0 (NCH₂), 66.6 (d, $^1J_{Rh-C} = 14$ Hz, COD), 69.4 (d, $^1J_{Rh-C} = 14$ Hz, COD), 73.8 (SiOC(CH₃)₃), 84.1 (OC(CH₃)₂(CH₂N)), 90.3 (Ta-CH₂^tBu), 95.0 (d, $^1J_{Rh-C} = 7.6$ Hz, CH_{COD}), 97.6 (d, $^1J_{Rh-C} = 7.6$ Hz, CH_{COD}), 123.9 (CH_{imid}), 124.1 (CH_{imid}), 128.5 (CH_{Ar}), 130.0 (CH_{Ar}), 135.6 (C_{Ar}), 138.0 (C_{Ar}), 138.2 (C_{Ar}), 139.3 (C_{Ar}), 184.7 (d, $^1J_{Rh-C} = 52$ Hz, Rh-C_{NHC}). DRIFT (25°C, KBr solid solution under argon) 2973.4 (s, ν_{C-H}), 2952.8 (s, ν_{C-H}), 2898.5 (m, ν_{C-H}), 2876.8 (m, ν_{C-H}), 2830.8 (m, ν_{C-H}), 1469.8 (m), 1404.3 (w), 1387.1 (m), 1363.5 (s), 1322.0 (w), 1291.4 (w), 1239.1 (m), 1230.3 (m), 1189.5 (m), 1159.3 (m), 1139.3 (w), 1063.0 (s), 1027.9 (w), 974.2 (w), 941.2 (s), 851.6 (w), 826.4 (w), 799.7 (m), 747.1 (w), 725.0 (w), 696.7 (m), 568.0 (w). Anal. calcd for C₅₁H₉₃ClN₂O₅SiTaRh: C, 52.71; H, 8.07; N, 2.41. Found: C, 52.62; H, 8.20; N, 2.55.

Conflicts of interest

There are no conflicts to declare.

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