Supporting Information for the paper entitled:

A Trigonal and Hindered Tertiary Phosphine Ligand Rendered Anionic by a Niobate Anchor: Formation of Zwritterionic M(I) (M= Cu, Ag, Au, Rh) Complexes

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S1 – Synthetic Procedures and Spectroscopic Data

S1.1 General Considerations

All manipulations were performed under an atmosphere of purified dinitrogen using a Vacuum Atmospheres glove box (model MO-40 M) or Schlenk techniques at room temperature unless otherwise stated. Methyliodide, purchased from Sigma-Aldrich, was purified by distillation. Anhydrous copper chloride, rhodium cyclooctadiene chloride dimer, and anhydrous silver triflate were purchased from Sigma-Aldrich and used as received. $[Na(Et_2O)][PNb(N[Np]Ar)_3]$ (Ar = 3.5-dimethylphenyl; Np = neo-pentyl)[1], diphenylketene[2] and Au(THT)Br[3] were synthesized according to literature methods. Solvents were obtained anhydrous and oxygen-free by bubble degassing (N_2) and purification through columns of alumina. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Benzene-d_6, toluene-d_8, $CDCl_3$ and THF-d_8 were degassed and stored over molecular sieves for at least 2 d prior to use. Celite 435 (EM Science) was dried by heating above 200 °C under a dynamic vacuum for at least 24 h prior to use. NMR spectra were obtained on Varian Mercury 300, Variana Inova 500, or Bruker Avance 400 instruments equipped with Oxford Instruments superconducting magnets and referenced to residual C_6H_5D (^1H = 7.16 ppm, ^{13}C = 128.06 ppm), $CD_2HC_6D_6$ (^1H = 2.09 ppm), C_4D_7HO (^1H = 3.58 ppm, ^{13}C = 25.31 ppm) or to tetramethylsilane as an internal standard in the case of $CDCl_3$ (^1H = 0 ppm, ^{13}C = 0 ppm). ^{31}P NMR spectra were referenced externally to 85% H_3PO_4 in D_2O. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Infrared spectra (thin films on KBr plates) were recorded on a Perkin-Elmer Model 2000 FTIR spectrometer under a N_2 purge at room temperature. Abbreviations for infrared intensity: s, strong; m, medium; w, weak; vw, very weak; br, broad. Elemental analyses were performed by Midwest Microlab LLC, Indianapolis, IN.

Synthesis of $[P(C[CPh_2]O)_2NbN[Np]Ar)_3][Na(THF)]$ ([Na(THF)][2]): To a thawing solution of $[Na(Et_2O)][PNb(N[Np]Ar)_3]$ ($[Na(OEt_2)]$[**1**]) (600 mg, 0.76 mmol) in Et_2O (5 mL) was added a solution of diphenylketene (295 mg, 1.52 mmol, 2 equiv.) in Et_2O.

After reaction at room temperature for 2 h the solvent was removed in vacuo and the residue suspended in 10 mL of pentane. The dark-red powder was isolated on a sintered glass frit and dried *in vacuo* to constant mass (700 mg, 78 %). The product can be recrystallized from a mixture of pentane and a little diethyl ether to give dark-red crystals (m. p.: 155 °C). ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 0.59 (s, 9H, *t*Bu), 0.67 (s, 18H, *t*Bu), 2.11 (s, 6H, ArCH_3), 2.40 (br d, 12H, ArCH_3), 3.57 (d, 2H, N-CH_2), 4.06 (s, 2H, N-CH_2), 4.45 (d, 2H N-CH_2), 6.22 (s, 1H, Ar), 6.70 (s, 2H, Ar), 7.05 (m, Ph), 7.29 (m, Ph), 7.55 (m, Ph), 7.86 (m, Ph). ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 20 °C): δ 21.5 (s, Ar*C*H_3), 21.7 (br s, Ar*C*H_3), 29.3 (s, C(*C*H_3)$_3$), 29.5 (s, C(*C*H_3)$_3$), 34.6 (s, *C*(CH_3)$_3$), 34.6 (s, *C*(CH_3)$_3$), 70.6 (br, N-*C*H_2), 120.7 (d, $^2J_{CP}$ = 19 Hz, Ph_2*C*CO), 124.5 (s, *C*H$_{\mathrm{Ar/Ph}}$), 124.5 (s, *C*H$_{\mathrm{Ar/Ph}}$), 125.2 (s, *o*-*C*H$_{\mathrm{Ar}}$), 125.3 (s, *C*H$_{\mathrm{Ar/Ph}}$), 125.5 (br, *o*-*C*H$_{\mathrm{Ar}}$), 126.0 (s, *C*H$_{\mathrm{Ar/Ph}}$), 128.0 (s, *C*H$_{\mathrm{Ph}}$), 130.4 (s, *C*H$_{\mathrm{Ph}}$), 132.9 (s, *C*H$_{\mathrm{Ph}}$), 132.9 (s, *C*H$_{\mathrm{Ph}}$), 137.1 (br, *m*-*C*$_{\mathrm{Ar}}$), 137.8 (s, *m*-*C*$_{\mathrm{Ar}}$), 142.3 (s, *i*-*C*$_{\mathrm{Ph}}$), 142.7 (d, $^3J_{CP}$ = 3 Hz, *i*-*C*$_{\mathrm{Ph}}$), 154.5 (s, *i*-*C*$_{\mathrm{Ar}}$), 156.3 (s, *i*-*C*$_{\mathrm{Ar}}$), 168.4 (d, $^1J_{CP}$ = 46 Hz, Ph_2C*C*O). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ −85.0 (s). IR (Et_2O solution, KBr plates, cm^{-1}): 3047 vw, 3025 vw, 2947 s, 2862 w, 1600 m, 1586 m, 1519 w, 1490 w, 1471 w, 1435 w, 1133 w, 1102 w, 1001 m, 758 m, 696 m, 682 m. Anal. Calc. (found) for $C_{71}H_{88}N_3O_3PNbNa$; C: 72.37 (71.95), H: 7.53 (7.79), N: 3.57 (3.49).

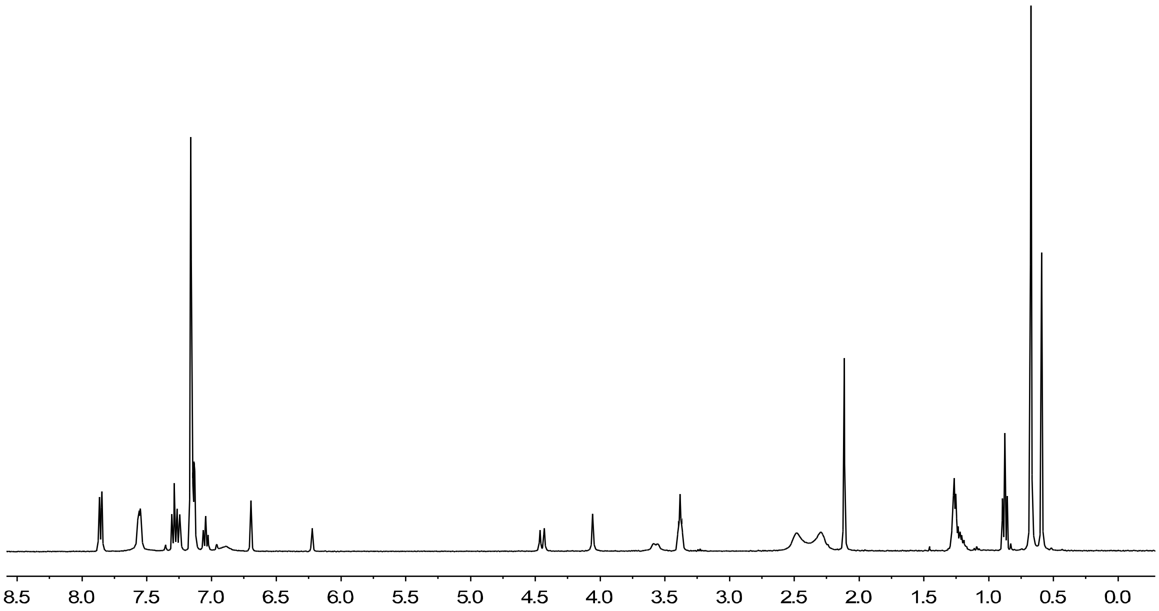

Figure 1. ^{1}H NMR spectrum of [Na(THF)][**2**] in d_6-benzene at ambient temperature (400 MHz).

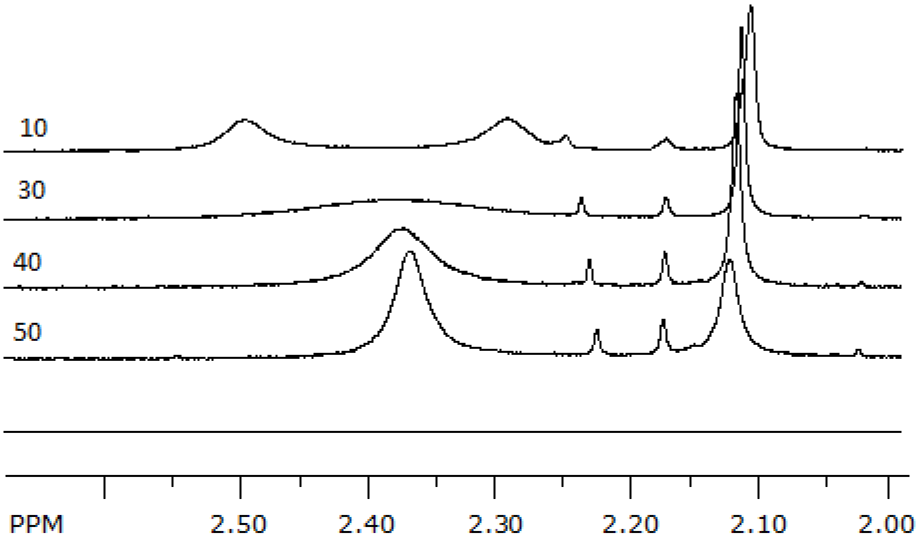

Figure 2. ^{1}H VT-NMR of [Na(THF)][**2**] (temperature shown in degrees Celsius along left edge), showing the anilide methyl peaks, which exhibit slow exchange at room temperature. (500 MHz, C_6D_6).

Synthesis of [P(C[CPh$_2$]O)$_3$Nb(N[Np]Ar)$_3$][Na(THF)$_n$] ([Na(THF)$_n$)]3) (n=1 or 6): ***a)*** A solution of [Na(THF)][**2**] (107 mg, 0.09 mmol) in Et_2O (4 mL) was treated with diphenylketene (17.6 mg, 0.09 mmol) at room temperature. The solution was stirred for 30 min to yield a fine, bright yellow precipitate. This was isolated on a frit, washed with diethyl ether and thoroughly dried *in vacuo* to an analytically pure yellow powder ([Na(THF)][**3**]) (107 mg, 0.079 mmol, 88%). ***b)*** To a solution of [Na(OEt$_2$)][**1**] (1.48 g, 1.87 mmol) in 20 mL of Et_2O and 2 mL of THF was added an ether solution of diphenylketene (1.1 g, 5.7 mmol, 3.0 equiv.) dropwise at room temperature. After 10 min a fine, pale yellow precipitate began to form. The reaction was allowed to proceed for one hour, and then the yellow powder was separated from the red solution by filtration over a glass frit. The powder was washed with cold diethyl ether and dried under vacuum, giving 2.35 g of [Na(THF)][**3**] (1.74 mmol, 93%). [Na(THF)$_6$][**3**] can be crystallized by slowly diffusing diethyl ether into a THF solution at room temperature to afford yellow crystals suitable for X-ray crystallography. Spectroscopic data is reported for [Na(THF)$_6$][**3**]. M. p.: > 250 °C. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 0.89 (s, 27H, *t*Bu), 1.40 (m, 24H, THF), 2.26 (s, 9H, Ar-CH_3), 2.57 (s, 9H, Ar-CH_3), 3.02 (d, $^2J_{HH}$ = 13 Hz, 3H, N-CH_2), 3.51 (m, 24H, THF), 4.68 (s, 3H, *o*-CH_{ar}), 5.47 (d, $^2J_{HH}$ = 13 Hz, 3H, N-CH_2), 6.38 (m, 3H,Ph), 6.57 (m, 6H, Ph), 6.81 (s, 3H, *p*-CH_{ar}), 7.09 (m, 6H, Ph), 7.45 (m, 6H, Ph), 7.55 (m, 3H, Ph), 7.71 (s, 3H, *o*-CH_{ar}), 8.22 (d, $^3J_{HH}$ = 8.2 Hz, 6H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 20 °C): δ 22.3 (s, Ar-CH$_3$), 22.3 (s, Ar-CH$_3$), 26.1 (s, THF), 30.0 (s, C(CH$_3$)$_3$), 36.5 (s, C(CH$_3$)$_3$), 68.2 (s, THF), 75.5 (N-CH$_2$), 121.4 (d, $^1J_{CP}$ = 39.9 Hz, C_2), 121.8 (s, *o*-CH$_{Ar}$), 123.7 (s), 125.4 (s, *p*-CH$_{Ar}$), 125.7 (s, CH$_{Ph}$), 127.8 (s, CH$_{Ph}$), 127.9 (s, CH$_{Ph}$), 128.5 (s, *o*-CH$_{Ar}$), 128.6 (s, CH$_{Ph}$), 128.7 (s, CH$_{Ph}$), 130.6 (s, CH$_{Ph}$), 134.1 (s, CH$_{Ph}$), 134.7 (s, CH$_{Ph}$), 134.8 (s, CH$_{Ph}$), 135.5 (s, *m*-C_{Ar}), 137.4 (s, *m*-C_{Ar}), 142.7 (d, $^2J_{CP}$ = 9.3 Hz, *i*-C_{Ph}), 149.3 (d, $^3J_{CP}$ = 10.7 Hz, *i*-C_{Ph}), 158.0 (s, *i*-C_{Ar}), 161.7 (s, C_1). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ −23.5 (s, $\nu_{1/2}$ = 105 Hz). IR (THF solution, KBr plates, cm^{-1}): 3047 sh, 2942 sh, 2874 sh, 1588 m, 1510 s, 1491 s, 1436 m, 1392 sh, 1260 m, 1224 w, 1136 w, 1119 w, 1053 s, 1001 m, 947 m, 900 m, 844 m, 763 m, 751 m, 697 s, 682 s. Anal. Calc. (found) for $C_{81}H_{90}N_3O_3PNaNb \cdot 6$ THF; C: 72.77 (72.54), H: 8.02 (7.73), N: 2.43 (2.39).

^{1}H NMR of [Na(THF)][**3**] (500 MHz, benzene-d_6, 20^o C): δ 0.90 (s, 27 H, *t*Bu), 2.27 (s, 9H, ArCH_3), 2.59 (s, 9H, ArCH_3), 3.03 (d, $^2J_{HH}$ = 13 Hz, 3H, N-CH_2), 4.69 (s, 3H, *o*-C$H_{Ar\backslash}$), 5.54 (d, $^2J_{HH}$ = 13 Hz, 3H, N-CH_2), 6.35 (t, $^3J_{HH}$ = 7 Hz, 3H, *p*-C$H_{\mathrm{Ph,\ up}}$), 6.50 (t, $^3J_{HH}$ = 7 Hz, 3H, *m*-C$H_{\mathrm{Ph,\ up}}$), 6.53 (t, $^3J_{HH}$ = 7 Hz, 3H, *m*-C$H_{\mathrm{Ph,\ up}}$), 6.82 (s, 3H, *p*-CH_{Ar}), 6.96 (d, $^3J_{HH}$ = 7 Hz, 3H, *o*-C$H_{\mathrm{Ph,\ up}}$), 7.09 (t, $^3J_{HH}$ = 7 Hz, 3H, *p*-C$H_{\mathrm{Ph,\ down}}$), 7.43 (d, $^3J_{HH}$ = 7 Hz, 3H, *o*-C$H_{\mathrm{Ph,\ up}}$), 7.46 (t, $^3J_{HH}$ = 7 Hz, 6H, *m*-C$H_{\mathrm{Ph,\ down}}$), 7.73 (s, 3H, o-CH_{Ar}), 8.20 (d, $^3J_{HH}$ = 7 Hz, 6H, *o*-C$H_{\mathrm{Ph,\ down}}$).

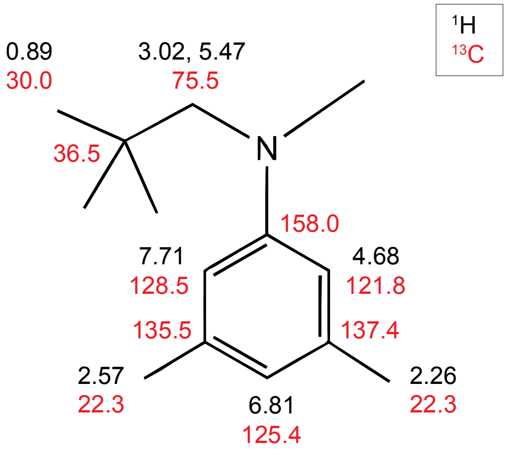

Figure 3. NMR assignment of the ^{1}H and ^{13}C NMR resonances of the anilide ligand. Note the different ^{1}H NMR chemical shifts of the *ortho* and the methylene protons arising from the sterically constrained conformation in solution.

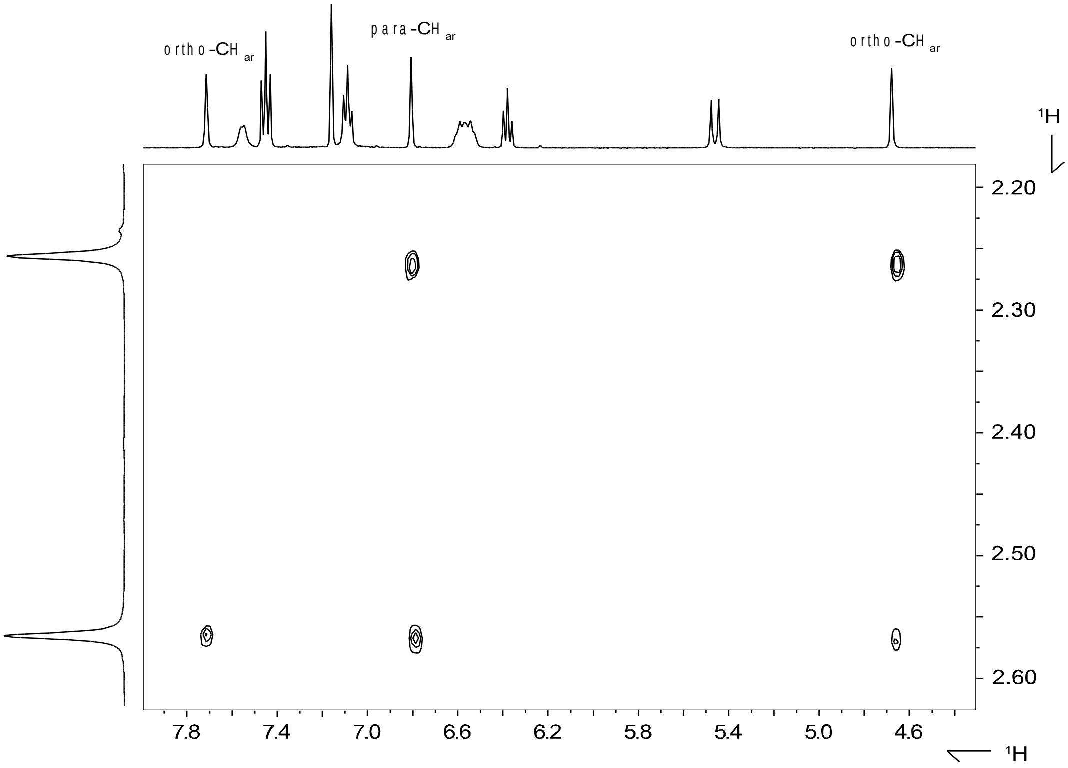

Figure 4. Section of the ^{1}H,^{1}H NOESY NMR spectrum of [Na(THF)$_6$][**3**] showing crosspeaks between the aromatic and methyl region of the anilide ligand (400 MHz, 293 K, d_6-benzene).

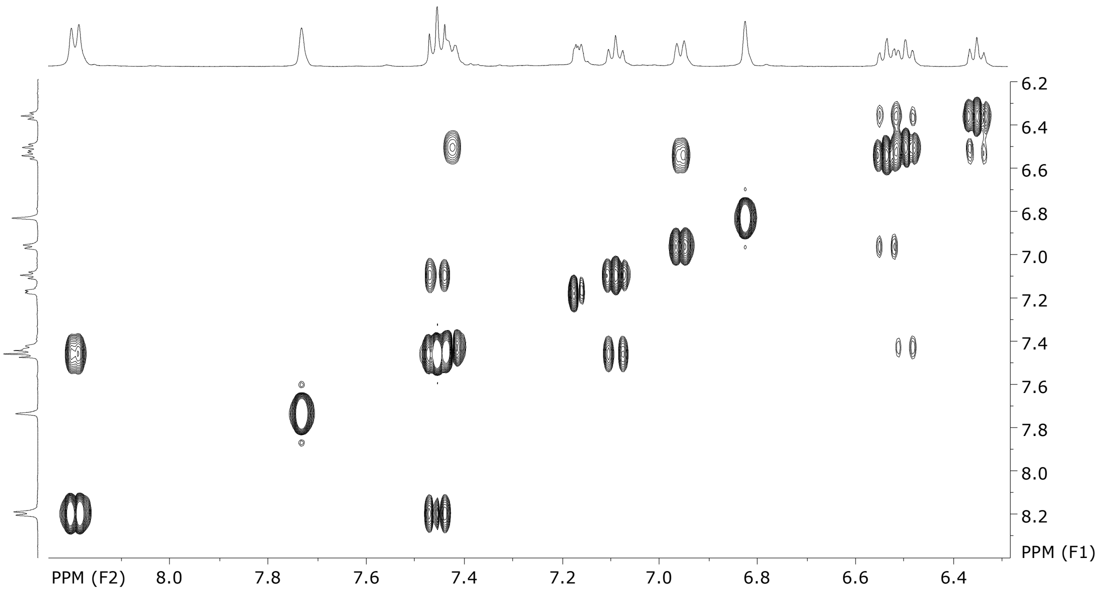

Figure 5 ^{1}H gCOSY showing couplings between protons on the phenyl rings of [Na(THF)][**3**].

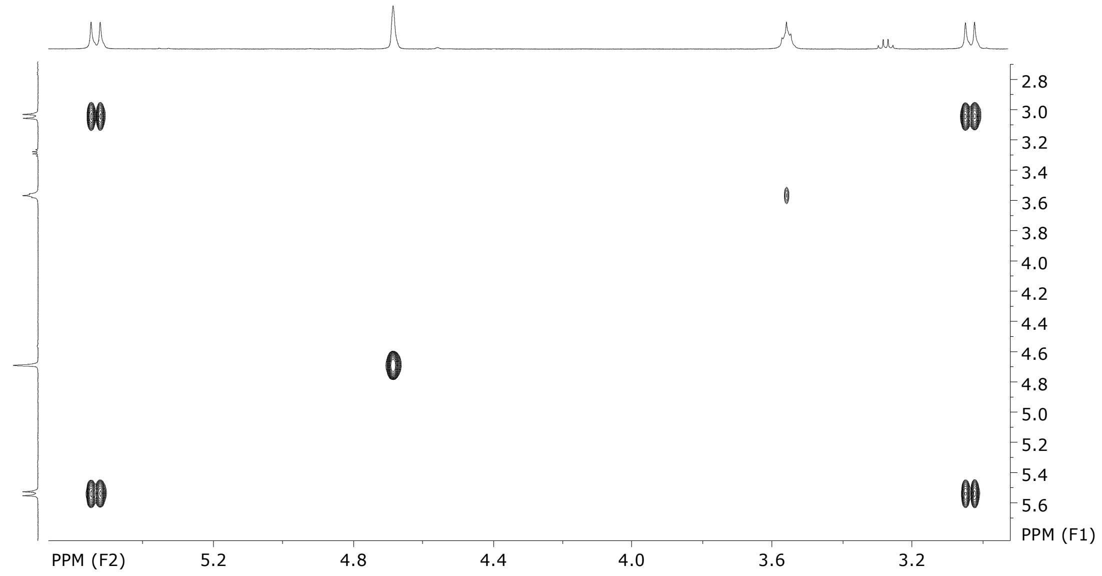

Figure 6. ^{1}H gCOSY showing geminal coupling between inequivalent methylene protons of the N-CH_2 groups on the anilide ligands.

Treatment of [Na(OEt$_2$)][1] with 0.9 Equivalents of Diphenylketene. [Na(OEt$_2$)][**1**] (50 mg, 0.063 mmol, 1.0 equiv.) was dissolved in diethyl ether and frozen. A solution of diphenylketene (11 mg, 0.058 mmol, 0.9 equiv.) in diethyl ether (1 mL) was added dropwise to the thawing solution of [Na(OEt$_2$)][**1**] over the course of ten minutes. The reaction was allowed to stir at room temperature for 20 minutes and then concentrated to dryness under vacuum. The red residue was analyzed by ^{31}P and ^{1}H NMR. ^{31}P NMR (121.6 MHz, benzene-*d*$_6$, 20^{O} C): δ = -85 (s, [Na(THF)][**2**]), 264 (s, putative single addition product). The ^{1}H NMR shows a number of broad, overlapping features in addition to the resonances of [Na(THF)][**2**].

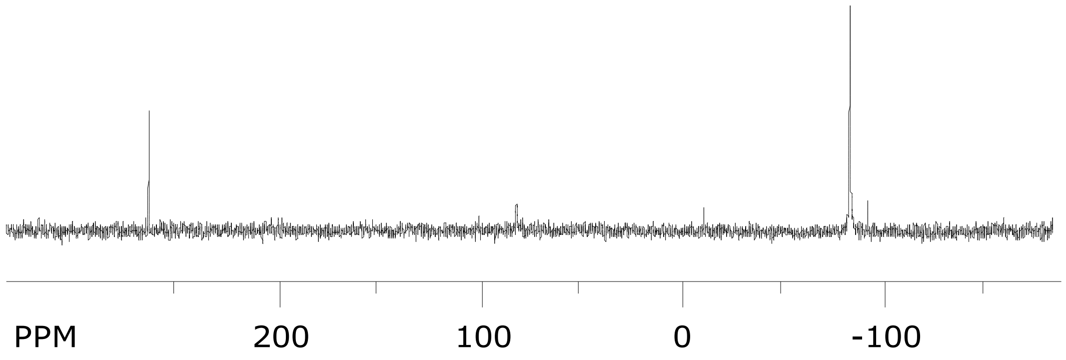

***Figure** 7*. ^{31}P NMR of the reaction between [Na(OEt$_2$)][**1**] and 0.9 equivalents of diphenylketene.

Synthesis of (THT)AuP(C[CPh$_2$]O)$_3$Nb(N[Np]Ar)$_3$ ((THT)Au[3]). a. [Na(THF)][**3**] (200 mg, 0.145 mmol, 1.0 equiv) and Au(THT)Cl (47 mg, 0.145 mmol, 1.0 equiv) were separately dissolved in THF (7 mL each) and frozen. The Au(THT)Cl solution was allowed to thaw and then added dropwise to the thawing solution of [Na(THF)][**3**], giving a yellow solution. No immediate change was observed. The reaction was allowed to stir at room temperature for 3 hours. After 30 minutes, the reaction mixture had turned dark red; after two hours, the mixture appeared cloudy, and the turbidity increased over the next hour. The reaction mixture was then dried under vacuum. The dark red residue was suspended in a mixture of pentane and diethyl ether, and a pale green/yellow solid was isolated by filtration over a glass frit and washed with pentane. The solid was taken up in minimal toluene and filtered to remove a gray-green solid. The yellow filtrate was concentrated to dryness to give 110 mg of (THT)Au[**3**] (0.070 mmols, 50%). Crystals suitable for x-ray diffraction where grown via vapor diffusion of pentane into a THF solution. **b.** [Na(THF)][**3**] (200 mg, 0.14 mmol, 1.0 equiv) and Au(THT)Br (48 mg, 0.14 mmol, 1.0 equiv) were separately dissolved in THF (5 mL each) and frozen. The thawing solution of Au(THT)Br was added dropwise to the frozen solution of [Na(THF)]**3** in five portions, allowing the mixture to thaw for five minutes between portions, and then freezing again. The reaction mixture took on a greenish hue. The reaction mixture was then allowed to thaw completely and then immediately filtered through celite, leaving NaBr as a gray solid which was washed with cold THF. The orange filtrate was concentrated and dissolved in minimal Et_2O, and a yellow solid was precipitated by addition of cold pentane. (THT)Au[**3**] was isolated as a yellow powder by isolation atop a sintered glass frit and washed with cold pentane (120 mg, .077 mmol, 55%). ^1H NMR (500 MHz, THF 20° C) $\delta = 0.85$ (s, 27H, *t*Bu), 1.03 (br. m, 4H, THT(2,3)), 1.86 (br. m, 4H, THT(1,4)), 2.21 (s, 9H, $ArCH_3$), 2.42 (s, 9H, $ArCH_3$), 3.21 (d, $^2J_{HH} = 13$ Hz, 3H, N-CH_2), 4.70 (s, 3H, *o*-CH_{Ar}), 4.99 (d, $^2J_{HH} = 13$ Hz, 3H, N-CH_2), 6.66 (t, $^3J_{HH} = 7$ Hz, 3H, *p*-$CH_{Ph, up}$), 6.75 (s, 3H, *p*-CH_{Ar}), 6.84 (t, $^3J_{HH} = 7$ Hz, 3H, *m*-$CH_{Ph, up}$), 6.91 (t, $^3J_{HH} = 7$ Hz, 3H, *m*-$CH_{Ph, up}$), 7.11 (t, $^3J_{HH} = 7$ Hz, 3H, *p*-$CH_{Ph, down}$), 7.42 (m, 9H, *m*-$CH_{Ph, down}$ and *o*-$CH_{Ph, up}$), 7.46 (s, 3H, *o*-CH_{Ar}), 7.80 (d, $^3J_{HH} = 7$ Hz, 3H, *o*-$CH_{Ph, up}$), 8.21 (d, $^3J_{HH} = 7$ Hz, 6H, *o*-$CH_{Ph, down}$). $^{13}C\{^1H\}$ NMR (125.7 MHz, THF, 20° C) $\delta = 21.7$ (s, $ArCH_3$), 21.9 (s, $ArCH_3$), 29.3 (s, THT(2,3)), 29.9 (s, $C(CH_3)_3$), 35.7 (s, $C(CH_3)_3$), 37.0 (s, THT(1,4)), 74.7 (s, N-CH_2), 121.4 (s, *o*-CH_{Ar}), 124.1 (d, $^2J_{CP} = 37$ Hz, Ph_2CCO), 125.3 (s, $CH_{Ph/Ar}$), 125.9 (s, $CH_{Ph/Ar}$), 125.9 (s, $CH_{Ph/Ar}$), 128.3 (s, $CH_{Ph/Ar}$), 128.6 (s, $CH_{Ph/Ar}$), 131.4 (s, $CH_{Ph/Ar}$), 133.3 (s, $CH_{Ph/Ar}$), 135.2 (br. s, CH_{Ph}), 135.4 (s, *m*-C_{Ar}), 136.9 (s, *m*-C_{Ar}), 143.2 (d, $^3J_{CP} = 11$ Hz, *i*-C_{Ph}), 145.3 (d, $^3J_{CP} = 6$ Hz, *i*-C_{Ph}), 156.7 (s, *i*-C_{Ar}), 156.9 (d, $^1J_{CP} = 55$ Hz, Ph_2CCO). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 20° C) δ 16 (s) ppm. FTIR (KBr plates) cm^{-1}: 3412 (br, m), 2918 (m), 2859 (w), 2279 (w), 2016 (w), 1957 (br, w), 1635 (w), 1436 (w), 1235 (w), 1215 (m), 1181 (w), 1106 (m), 1070 (w), 1030 (m), 994 (m), 942 (m), 927 (m), 897 (m), 847 (m), 808 (m), 767 (s), 754 (s), 695 (s), 682 (s), 655 (m), 617 (s), 525 (s), 495 (s), 467 (s), 438 (m), 425 (m). Anal. Calc. (found) for $C_{85}H_{98}N_3O_3SNbPAu$; C: 65.33 (65.40), H: 6.32 (6.70), N: 2.69 (2.58).

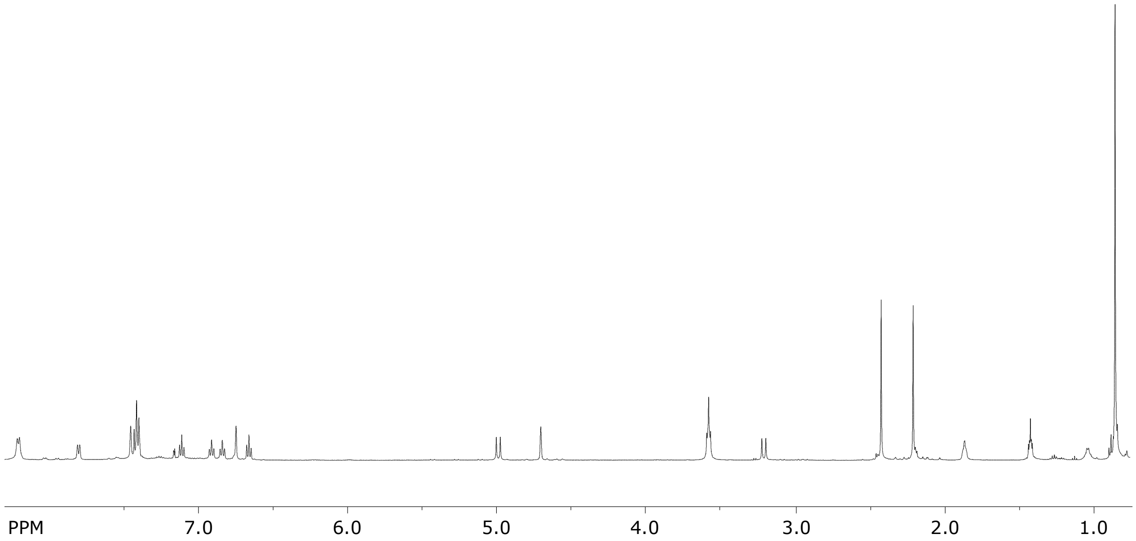

Figure 8. ^{1}H NMR spectrum of (THT)Au[**3**] at 500 MHz in benzene-d_6 at ambient temperature.

Synthesis of (py)AuP(C[CPh$_2$]O)$_3$Nb(N[Np]Ar)$_3$ ((py)Au[3]). **a.** (THT)Au[**3**] (25 mg, 0.014 mmol) was dissolved in 2 mL of pyridine and stirred at room temperature for one hour. The reaction mixture was filtered through celite and concentrated under vacuum. The yellow-orange solution had darkened slightly. The sample was dissolved in minimal THF; 5 mL of pentane were added and the solution was stored in the freezer to precipitate an orange-red solid which was shown by NMR to be (py)Au[**3**]. **b.** [Na(THF)][**3**] (105 mg, 0.068 mmol, 1.0 equiv.) was dissolved in pyridine (1 mL), and Au(THT)Br (25 mg, 0.069 mmol, 1.0 equiv.) was dissolved in THF (2 mL). Both solutions were frozen. The solution of Au(THT)Br was allowed to thaw and was added dropwise, slowly, to the thawing solution of [Na(THF)]**3**. The reaction mixture was allowed to thaw completely and stir at room temperature for 3 hours, over which time the initially orange-yellow solution turned dark red. The reaction mixture was concentrated to dryness, redissolved in minimal toluene (1 mL) and filtered through Celite in a pipette filter. NaBr was isolated on the filter as a black solid, and the dark red filtrate was dried under vacuum, giving an orange-yellow residue. The residue was taken up in diethyl ether (3 mL), then 3 mL of pentane were added to precipitate an orange solid which was collected by filtration on a glass frit and washed with pentane. A second crop was collected by taking up the red filtrate in a 3:1 pentane:THF mixture and storing it in the freezer for 1 hour. 90 mg of (py)Au[**3**] were collected (0.058 mmol, 85%). Crystals suitable for x-ray diffraction were grown via vapor diffusion of pentane into a concentrated THF solution. ^{1}H NMR (400 MHz, C_6D_6, 20° C): δ = 0.88 (s, 27H, *t*Bu), 2.22 (s, 9H, ArC*H*$_3$), 2.44 (s, 9H, ArC*H*$_3$), 3.21 (d, $^2J_{HH}$ = 13 Hz, 3H, N-C*H*$_2$), 4.71 (s, 3H, *o*-C*H*$_{Ar}$), 5.05 (d, $^2J_{HH}$ = 13 Hz, 3H, N-C*H*$_2$), 6.16 (t, $^3J_{HH}$ = 7 Hz, 2H, *m*-C*H*$_{pyr}$), 6.47 (t, $^3J_{HH}$ = 7 Hz, 3H, C*H*$_{Ph}$), 6.61 (t, $^3J_{HH}$ = 7 Hz, 1H, *p*-C*H*$_{Ar}$), 6.70 (t, $^3J_{HH}$ = 7 Hz, 3H, C*H*$_{Ph}$) 6.72 (m, 2H, *o*-C*H*$_{pyr}$), 6.76 (s, 3H, *p*-C*H*$_{Ar}$), 6.88 (t, $^3J_{HH}$ = 7 Hz, 3H, C*H*$_{Ph}$), 7.11 (t, $^4J_{HH}$ = 7 Hz, 3H, C*H*$_{Ph}$), 7.39 (d, $^3J_{HH}$ = 7 Hz, 3H, *o*-C*H*$_{Ph,\ up}$), 7.43 (t, $^3J_{HH}$ = 7 Hz, 6H, *m*-C*H*$_{Ph,\ down}$), 7.51 (s, 3H, *o*-C*H*$_{Ar}$), 7.87 (d, $^3J_{HH}$ = 7 Hz, 3H, *o*-C*H*$_{Ph,\ up}$), 8.25 (d, $^3J_{HH}$ = 7 Hz, 6H, *o*-C*H*$_{Ph,\ down}$). ^{13}C{^{1}H} (100.6 MHz, THF-d_8, 20° C) δ = 21.6 (s, Ar*C*H$_3$), 21.8 (s, Ar*C*H$_3$), 29.9 (s, C(*C*H$_3$)$_3$), 35.8 (s, *C*(CH$_3$)$_3$), 74.9 (s, N-*C*H$_2$), 111.2 (s, *C*H$_{Ph}$), 121.8 (s, *o*-*C*H$_{Ar}$), 124.6 (d, $^2J_{CP}$ = 36 Hz, Ph$_2$*C*CO), 125.2 (s, *C*H$_{Ph/Ar}$), 125.5 (d, $^4J_{PC}$ =2 Hz, *m*-*C*H$_{pyr}$), 125.8 (s, *C*H$_{Ph/Ar}$), 126.7 (s, *C*H$_{Ar/Ph}$), 128.2 (s, *C*H$_{Ph/Ar}$), 128.6 (s, *C*H$_{Ph/Ar}$), 128.8 (s, *C*H$_{Ph/Ar}$), 131.7 (s, *C*H$_{Ph/Ar}$), 133.5 (s, *C*H$_{Ph/Ar}$), 135.6 (s, *m*-*C*H$_{Ar}$), 135.6 (s, *p*-*C*H$_{pyr}$), 137.0 (s, *m*-*C*H$_{Ar}$), 140.8 (s, *C*H$_{Ph/Ar}$), 143.9 (d, $^3J_{PC}$ = 12 Hz, *i*-*C*$_{Ph}$), 145.6 (d, $^3J_{PC}$ = 6 Hz, *i*-*C*$_{Ph}$), 151.6 (d, $^3J_{PC}$ = 2 Hz, *o*-*C*H$_{pyr}$), 156.3 (d, $^1J_{PC}$ = 59 Hz, Ph$_2$C*C*O). ^{31}P{^{1}H} NMR (121.5 MHz, benzene-d_6, 20° C): δ = 6.9 (s) ppm. FTIR (KBr plates) cm^{-1}: 3300 (br, w), 2918 (br, w), 1576 (w), 1522 (w), 1285 (w), 1248 (m), 1127 (m), 1073 (w), 1041 (w), 995 (m), 944 (m), 903 (m), 839 (w), 796 (m), 765 (m), 753 (s), 729 (m), 693 (s), 680 (s), 656 (s), 620 (s), 533 (s), 466 (s). Anal. Calc. (found) for $C_{86}H_{95}N_4O_3NbPAu$; C: 66.48 (66.60), H: 6.16 (6.27), N: 3.61 (3.40).

Synthesis of (py)AgP(C[CPh$_2$]O)$_3$Nb(N[Np]Ar)$_3$ ((py)Ag[3]). Silver triflate (75 mg, 0.29 mmol, 1.1 equiv.) was suspended in pentane (30 mL) and frozen. [Na(THF)][**3**] (404 mg, 0.29 mmol, 1.0 equiv) was dissolved in pyridine (5 mL; required about 15 minutes of stirring to go into solution) to give a dark orange-brown solution which was also frozen. The silver triflate suspension was allowed to thaw, and the thawing solution of [Na(THF)][**3**] was added to it dropwise over the course of about 5 minutes. The reaction mixture, which appeared a cloudy pale orange, was allowed to stir for approximately 2 minutes after the addition was complete and then was filtered through Celite, washing with minimal benzene. Some light gray solid (sodium triflate) was recovered on the filter bed. The yellow-orange filtrate was concentrated to dryness, triturating twice with hexanes. The resulting yellow-orange powdery residue was taken up in ether, giving a dark orange solution; this solution was stored at -35° C for 30 minutes. (py)Ag[**3**] was precipitated as a yellow-orange powder and collected by filtration over a glass frit, washing with cold diethyl ether (370 mg over two crops, 0.25 mmol, 86%). ^{1}H NMR (300 MHz, benzene-d_6, 20° C) $\delta = 0.89$ (s, 27H, *t*Bu), 2.24 (s, 9H, ArCH_3), 2.49 (s, 9H, ArCH_3), 3.12 (d, $^2J_{\mathrm{HH}} = 13$ Hz, 3H, N-CH_2), 4.69 (s, 3H, *o*-CH_{Ar}), 5.17 (d, $^2J_{\mathrm{HH}} = 13$ Hz, 3H, N-CH_2), 6.23 (br, 2H, *m*-CH_{pyr}), 6.35 (t, $^3J_{\mathrm{HH}} = 7$ Hz, 3H, *p*-C$H_{\mathrm{Ph,\,up}}$), 6.65 (t, $^3J_{\mathrm{HH}} = 7$ Hz, 3H, *m*-C$H_{\mathrm{Ph,\,up}}$), 6.67 (br, 1H, *p*-CH_{pyr}), 6.78 (s, 3H, *p*-CH_{Ar}), 6.81 (t, $^3J_{\mathrm{HH}} = 7$ Hz, 3H, *m*-C$H_{\mathrm{Ph,\,up}}$), 6.91 (br, 2H, *o*-CH_{pyr}), 7.11 (t, $^3J_{\mathrm{HH}} = 7$ Hz, 3H, *p*-C$H_{\mathrm{Ph,\,down}}$), 7.33 (d, $^3J_{\mathrm{HH}} = 7$ Hz, 3H, *o*-C$H_{\mathrm{Ph,\,up}}$), 7.43 (t, $^3J_{\mathrm{HH}} = 7$ Hz, 6H, *m*-C$H_{\mathrm{Ph,\,down}}$), 7.60 (s, 3H, *o*-CH_{Ar}), 7.86 (d, $^3J_{\mathrm{HH}} = 7$ Hz, 3H, *o*-C$H_{\mathrm{Ph,\,up}}$), 8.23 (d, $^3J_{\mathrm{HH}} = 7$ Hz, 6H, *o*-C$H_{\mathrm{Ph,\,down}}$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 20° C): $\delta = 21.3$ (s, ArCH$_3$), 21.4 (s, ArCH$_3$), 29.0 (s, C(CH$_3$)$_3$), 35.0 (s, C(CH$_3$)$_3$), 74.1 (s, N-CH$_2$), 120.7 (s, *o*-CH$_{\mathrm{Ar}}$), 122.8 (d, $^2J_{\mathrm{CP}} = 38$ Hz, Ph$_2$$C$CO), 123.7 (br s, *m*-CH$_{\mathrm{pyr}}$), 124.1 (s, *p*-$CH_{\mathrm{Ar}}$), 124.9 (s, *p*-CH$_{\mathrm{Ph,\,down}}$), 125.7 (s, *p*-CH$_{\mathrm{Ph,\,up}}$), 127.2 (s, *o*-$CH_{\mathrm{Ar}}$), 127.4 (s, *m*-$CH_{\mathrm{Ph,\,down}}$), 127.8 (s, *m*-$CH_{\mathrm{Ph,\,up}}$), 128.0 (s, *m*-$CH_{\mathrm{Ph,\,up}}$), 130.9 (s, *o*-$CH_{\mathrm{Ph,\,down}}$), 132.1 (s, *o*-$CH_{\mathrm{Ph,\,up}}$), 133.6 (d, $J_{\mathrm{AgC}} = 6.0$ Hz, *o*-CH$_{\mathrm{Ph,\,up}}$), 134.6 (s, *m*-C_{Ar}), 136.2 (s, *m*-C_{Ar}), 138.6 (br. s, *p*-CH$_{\mathrm{pyr}}$), 142.6 (d, $^3J_{\mathrm{CP}} = 10.0$ Hz, *i*-$C_{\mathrm{Ph,\,down}}$), 145.9 (dd, $^3J_{\mathrm{CP}} = 9.3$ Hz, $J_{\mathrm{AgC}} = 1.1$ Hz, *i*-$C_{\mathrm{Ph,\,up}}$), 151.0 (br, *o*-CH$_{\mathrm{pyr}}$), 156.2 (s, *i*-C_{Ar}), 157.8 (dd, $^1J_{\mathrm{CP}} = 31$ Hz, $^2J_{\mathrm{AgC}} = 11$ Hz, Ph$_2$CCO). ^{31}P{^{1}H} NMR (121.5 MHz, benzene-d_6, 20° C) $\delta = -8$ (two doublets, ^1J(P-^{107}Ag) = 670 Hz, ^1J(P-^{109}Ag) = 780 Hz). FTIR (KBr plates), cm^{-1}: 3383 (br, w), 3050 (w), 2945 (m), 2863 (w), 2236 (w), 2081 (w), 1588 (m), 1562 (w), 1535 (s), 1516 (m), 1473 (w), 1439 (s), 1393 (m), 1366 (w), 1314 (m), 1287 (w), 1259 (s), 1226 (m), 1134 (s), 1119 (m), 1072 (w), 1045 (m), 1002 (m) 943 (m), 906 (m, 847 (m), 765 (m), 756 (m), 697 (s), 699 (s), 549 (m), 618 (m), 607 (w), 52 (w), 533 (w), 500 (m), 476 (m), 465 (m), 453 (s), 429 (m). Anal. Calc. (found) for

$C_{86}H_{95}N_4O_3NbPAg$; C: 70.29 (70.27), H: 6.86 (6.53), N: 3.81 (3.66).

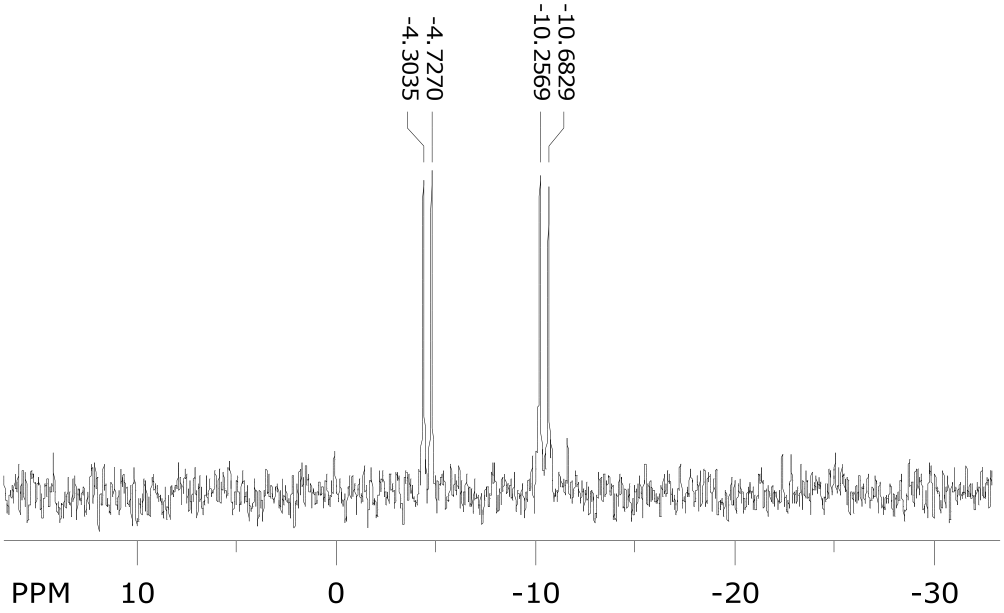

Figure 9. ^{31}P NMR spectrum of (py)Ag[**3**] at 121.6 MHz in $CDCl_3$, showing well-resolved coupling to ^{107}Ag and ^{109}Ag.

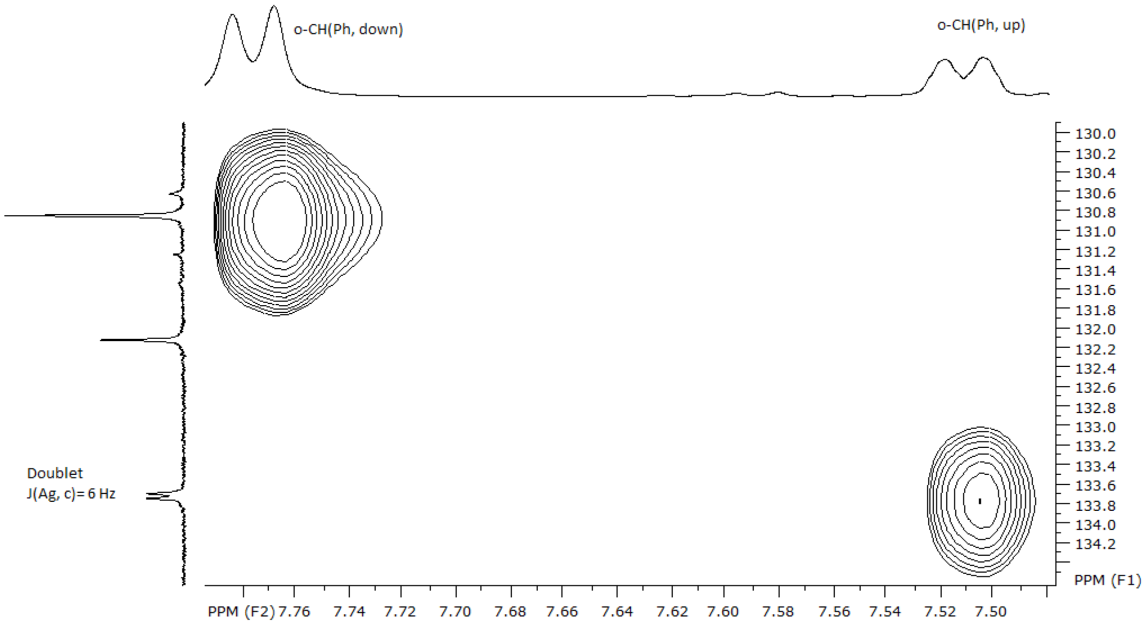

Figure 10. Section of the 2D HMQC spectrum of (py)Ag[**3**] in $CDCl_3$ which demonstrates that one of the *ortho* carbons of the "up" phenyl rings exhibits coupling to

silver.

Synthesis of (py)CuP(C[CPh$_2$]O)$_3$Nb(N[Np]Ar)$_3$ ((py)Cu[3]). [Na(THF)][**3**] (200 mg, 0.15 mmol) was suspended in toluene (15 mL) to give a cloudy yellow-orange mixture. Copper (I) chloride was also suspended in toluene (5 mL). A solution of pyridine (12 mg) in toluene (2 mL) was added to the copper chloride suspension, and all reagents were combined in a Schlenk bomb. No immediate change occurred. The reaction mixture was heated at 60° C while stirring for one hour. During this time the solution turned clear and darkened to dark orange; a grayish white crystalline precipitate formed. The reaction mixture was cooled to room temperature and filtered through Celite to remove NaCl; the filrate was clear and orange-yellow. The filtrate was concentrated under vacuum and the orange residue was redissolved in minimal THF. Pentane was added to crash out a yellow solid and the mixture was cooled to -40°C. (py)Cu[**3**] was collected as a bright yellow powder via filtration over a glass frit and washed with cold diethyl ether. Three crops were collected via concentration and reprecipitation of the filtrate to give 173 mg of product (0.12 mmol, 80%). Single crystals suitable for X-ray diffraction were grown via vapor diffusion of pentane into a concentrated THF solution at room temperature. ^{1}H NMR (500 MHz, THF-d_8, 20° C) $\delta = 0.33$ (s, 27H, *t*Bu), 1.96 (s, 9H, ArCH_3), 2.21 (s, 9H, ArCH_3), 2.59 (d, $^2J_{\mathrm{HH}} = 13$ Hz, 3H, N-CH_2), 4.20 (s, 3H, *o*-CH_{Ar}), 4.65 (d, $^2J_{\mathrm{HH}} = 13$ Hz, 3H, N-CH_2), 6.52 (s, 3H, *p*-CH_{Ar}), 6.61 (t, $^3J_{\mathrm{HH}} = 7$ Hz, 3H, *p*-CH_{Ph}), 6.81 (d, $^3J_{\mathrm{HH}} = 7$ Hz, 2H, *o*-CH_{pyr}), 6.91 (br, 3H, *m*-C$H_{\mathrm{Ph,\,up}}$), 7.03 (t, $^3J_{\mathrm{HH}} = 7$ Hz, 3H, *p*-CH_{Ph}), 7.09 (br, 3H, *m*-C$H_{\mathrm{Ph,\,up}}$), 7.10 (s, 3H, *o*-CH_{Ar}), 7.14 (t, $^3J_{\mathrm{HH}} = 7$ Hz, 2H, *m*-CH_{pyr}), 7.22 (t, $^3J_{\mathrm{HH}} = 7$ Hz, 6H, *m*-C$H_{\mathrm{Ph,\,down}}$), 7.26 (br, 3H, *o*-C$H_{\mathrm{Ph,\,up}}$), 7.56 (br, 3H, *o*-C$H_{\mathrm{Ph,\,up}}$), 7.70 (d, $^3J_{\mathrm{HH}} = 7$ Hz, 6H, *o*-C$H_{\mathrm{Ph,\,down}}$), 7.75 (t, $^3J_{\mathrm{HH}} = 7$ Hz, 1H, *p*-CH_{pyr}). ^{13}C{^{1}H} NMR (125.7 MHz, THF, 20° C) $\delta = 21.6$ (s, Ar*C*H$_3$), 21.8 (s, Ar*C*H$_3$), 29.8 (s, C(*C*H$_3$)$_3$), 35.9 (s, *C*(CH$_3$)$_3$), 75.0 (s, N-*C*H$_2$), 121.8 (s, *o*-*C*H$_{\mathrm{Ar}}$), 124.0 (s, *m*-*C*H$_{\mathrm{pyr}}$), 124.3 (d, $^1J_{\mathrm{CP}} = 37$ Hz, Ph$_2$*C*CO), 125.1 (s, *p*-*C*H$_{\mathrm{Ar}}$), 125.7 (s, *C*H$_{\mathrm{Ph/Ar}}$), 126.8 (s, *C*H$_{\mathrm{Ph/Ar}}$), 128.2 (s, *C*H$_{\mathrm{Ar/Ph}}$), 128.3 (s, *C*H$_{\mathrm{Ph/Ar}}$), 129.4 (br. s, *C*H$_{\mathrm{Ph/Ar}}$), 131.7 (s, *C*H$_{\mathrm{Ph/Ar}}$), 133.1 (br. s, *C*H$_{\mathrm{Ph/Ar}}$), 133.6 (br. s, *C*H$_{\mathrm{Ph/Ar}}$), 135.4 (s, *m*-*C*$_{\mathrm{Ar}}$), 137.0 (s, *m*-*C*$_{\mathrm{Ar}}$), 139.8 (s, *p*-*C*H$_{\mathrm{pyr}}$), 143.7 (d, $^3J_{\mathrm{CP}} = 10$ Hz, *i*-*C*$_{\mathrm{Ph}}$), 145.6 (d, $^3J_{\mathrm{CP}} = 8$ Hz, *i*-*C*$_{\mathrm{Ph}}$), 151.0 (s, *o*-*C*H$_{\mathrm{pyr}}$), 157.3 (s, *i*-*C*$_{\mathrm{Ar}}$), 157.8 (d, $^1J_{\mathrm{CP}} = 39$ Hz, Ph$_2$C*C*O). ^{31}P{^{1}H} NMR (121.6 MHz, benzene-d_6) $\delta = -10$ (s). FTIR (KBr plates) cm^{-1}: 3393 (br, w), 2917 (br, w), 1585 (w), 1512 (m), 1489 (m), 1436 (m), 1391 (m), 1362 (m), 1313 (w), 1284 (w), 1257 (m), 1226 (m), 1130 (m), 1118 (m), 1071 (w), 1033 (m), 996 (m), 943 (m), 901 (w), 877 (w), 845 (w), 802 (w), 764 (w), 752 (s), 729 (m), 695 (s), 675 (s), 657 (s), 617 (m), 04 (w), 552 (w), 531 (m). Anal. Calc. (found) for $C_{86}H_{95}N_4O_3NbPCu$; C: 72.73 (72.69), H: 6.74 (6.75), N: 3.95 (3.91).

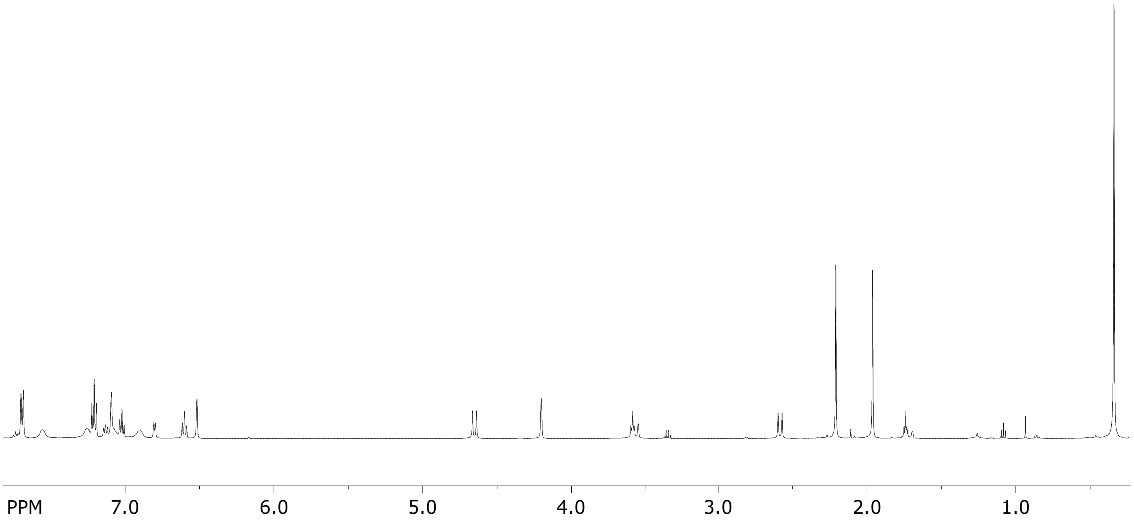

Figure 11. ^{1}H NMR spectrum of (py)Cu[**3**] at 500 MHz in THF-d_8 at ambient temperature. The broadened resonances in the aromatic region correspond to the "up" phenyl rings.

Synthesis of Rh[η^6-Ph,η^2- Ph-P[C(CPh$_2$)O]$_3$]Nb(N[Np]Ar)$_3$ (Rh[3]). [Na(THF)][**3**] (300 mg, 0.23 mmol, 1.0 equiv.) was suspended in benzene (15 mL) to give a cloudy yellow-orange mixture and frozen. Similarly, pyridine (24 mg, 0.30 mmol, 1.3 equiv.) was combined with 5 mL of benzene and frozen, and $[Rh(COD)Cl]_2$ (62 mg, 0.30 mmol, 1.3 equiv.) was dissolved in 5 mL of benzene to give a light orange solution and frozen. The thawing solution of $[Rh(COD)Cl]_2$ was added to the thawing solution of [Na(THF)] [**3**]. No observable change occurred. Once the reaction mixture had thawed fully, the thawing pyridine solution was added dropwise. Again, no observable change occurred. The reaction mixture was allowed to stir at room temperature for two hours, during which time it darkened slightly in color. Then, the reaction mixture was heated to 60° C for 30 minutes; the solution turned clear and dark red-orange. The reaction mixture was cooled to room temperature and filtered through Celite, leaving some gray-white solid. The red-orange filtrate was concentrated to dryness and redissolved in minimal toluene (1 mL); pentane was added (10 mL) and the mixture was cooled to -40° C to precipitate 235 mg (0.17 mmol, 74%) of Rh[**3**] as a yellow-orange powder which was collected by filtration over a glass frit, and washed with a cold 10:1 pentane:toluene mixture. Single crystals suitable for X-ray diffraction were grown via vapor diffusion of pentane into a concentrated THF solution. ^{1}H NMR (500 MHz, benzene-d_6, 20° C) $\delta = 0.85$ (s, 27H, *t*Bu), 2.22 (s, 9H, ArCH_3), 2.54 (s, 9H, ArCH_3), 2.98 (d, $^2J_{HH} = 13$ Hz, 3H, N-CH_2), 4.63 (s, 3H, *o*-CH_{Ar}), 5.53 (d, $^2J_{HH} = 13$ Hz, 3H, N-CH_2), 6.02 (t, $^3J_{HH} = 8$ Hz, 3H, *p*-C$H_{Ph, up}$), 6.43 (br., 6H, *m*-C$H_{Ph, up}$), 6.56 (br. d, $^3J_{HH} = 7$ Hz, 6H, *o*-C$H_{Ph, up}$), 6.80 (s, 3H, *p*-CH_{Ar}), 7.07 (t, $^3J_{HH} = 7$ Hz, 3H, *p*-C$H_{Ph, down}$), 7.41 (t, $^3J_{HH} = 7$ Hz, 6H, *m*-C$H_{Ph, down}$), 7.67 (s, 3H, *o*-CH_{Ar}), 8.06 (d, $^3J_{HH} = 7$ Hz, 6H, *o*-C$H_{Ph, down}$). ^{13}C{^{1}H} NMR (125.7 MHz, benzene-d_6, 20° C): $\delta = 21.9$ (s, ArCH$_3$), 22.0 (s, ArCH$_3$), 29.7 (s, C(CH$_3$)$_3$), 36.2 (s, C(CH$_3$)$_3$), 75.5 (s, N-CH$_2$), 110 (v. br., *o*-CH$_{Ph, up}$, from HMQC), 117.8 (br, *i*-$C_{Ph, up}$), 120.9 (s, *o*-CH$_{Ph}$), 121.3 (s, *p*-CH$_{Ph, up}$), 121.8 (d, $^2J_{PC} = 39$ Hz, Ph$_2$$C$CO), 123 (v. br., *o*-$CH_{Ph, up}$, from HMQC), 123 (v. br., *m*-CH$_{Ph, up}$, from HMQC), 125.4 (s, *p*-CH$_{Ar}$), 126.1 (s, *p*-CH$_{Ph, down}$), 127.5 (s, *m*-CH$_{Ph, down}$), 128.4 (s, *o*-CH$_{Ph, down}$), 129.0 (s, *o*-CH$_{Ar}$), 135.3 (s, *m*-CH$_{Ar}$), 137.3 (s, *m*-CH$_{Ar}$), 140.5 (d, $^3J_{CP} = 15$ Hz, *i*-$C_{Ph, down}$), 157.5 (s, *i*-C_{Ar}), 158.8 (d, $^1J_{CP} = 50$ Hz, Ph$_2$CCO). ^{31}P{^{1}H} NMR (121.6 MHz, benzene-d_6, 20° C) $\delta = 56$ (s, $^2J_{RhP} = 168$ Hz). FTIR (KBr plates) cm^{-1}: 3423 (br, m), 3051 (w), 2497 (m), 2862 (w), 2006 (w), 1960 (br, w), 1600 (m), 1575 (w), 1550 (m), 1491 (m), 1473 (w), 1439 (s), 1394 (w), 1363 (w), 1320 (m), 1305 (w), 1286 (w), 1260 (m), 1223 (m), 1181 (w), 1132 (s), 1069 (m), 1042 (m), 1001 (m) 949 (m), 932 (w), 905 (m), 847 (w), 819 (w), 757 (s), 695 (s), 685 (s), 658 (m), 614 (m), 571 (w), 542 (m), 470 (m), 449 (w). Anal. Calc. (found) for $C_{81}H_{90}N_4O_3NbPRh$; C: 70.47 (70.42), H: 6.57 (6.53), N: 3.04 (3.00).

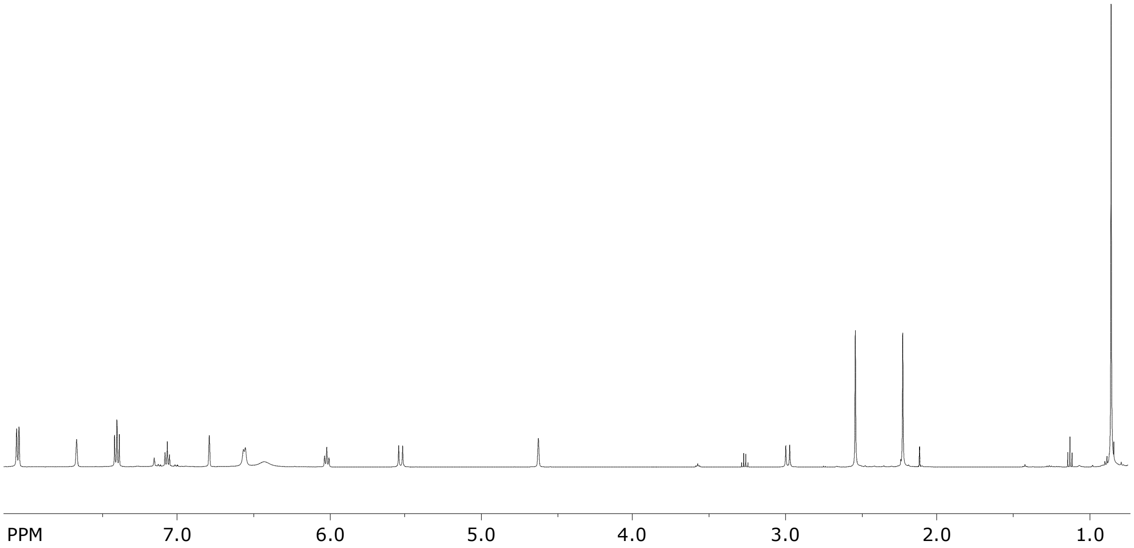

Figure 12. ^{1}H NMR spectrum of Rh[**3**] at 500 MHz in benzene-d_6. The broadened resonances in the aromatic region correspond to the "up" phenyl rings.

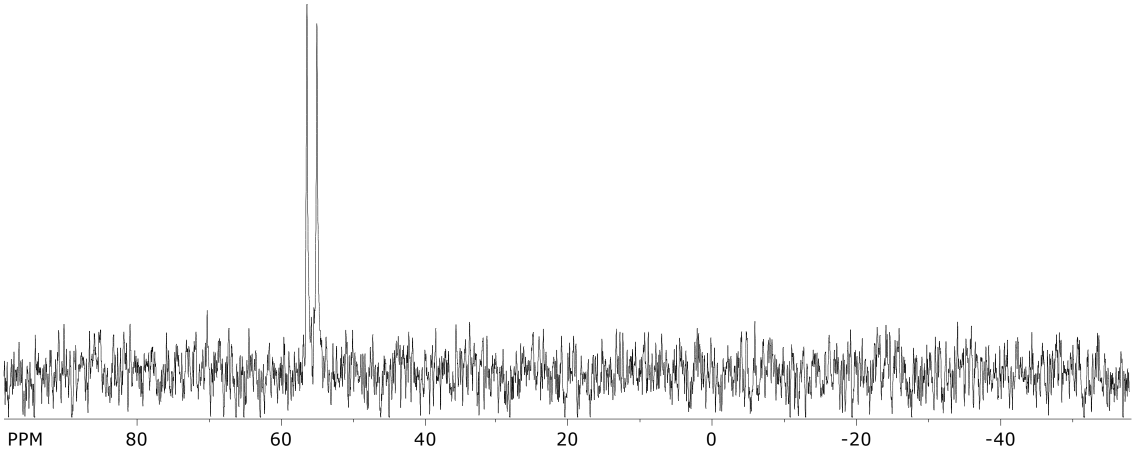

Figure 13. ^{31}P NMR spectrum of Rh[**3**] at 121.6 MHz in benzene-d_6, showing rhodium-phosphorus coupling.

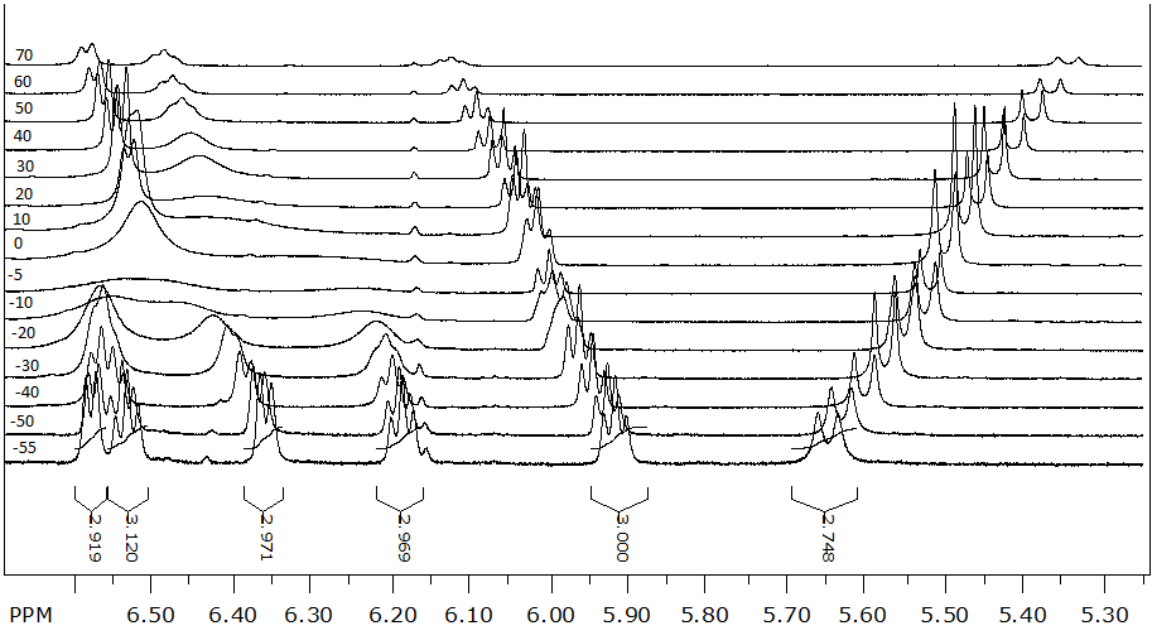

Figure 14. Section of the variable-temperature ^{1}H NMR of Rh[3] in toluene-d_8 at 500 MHz, showing the resonances corresponding to the protons of the "up" phenyl rings. Temperature is shown in degrees Celsius along the left edge.

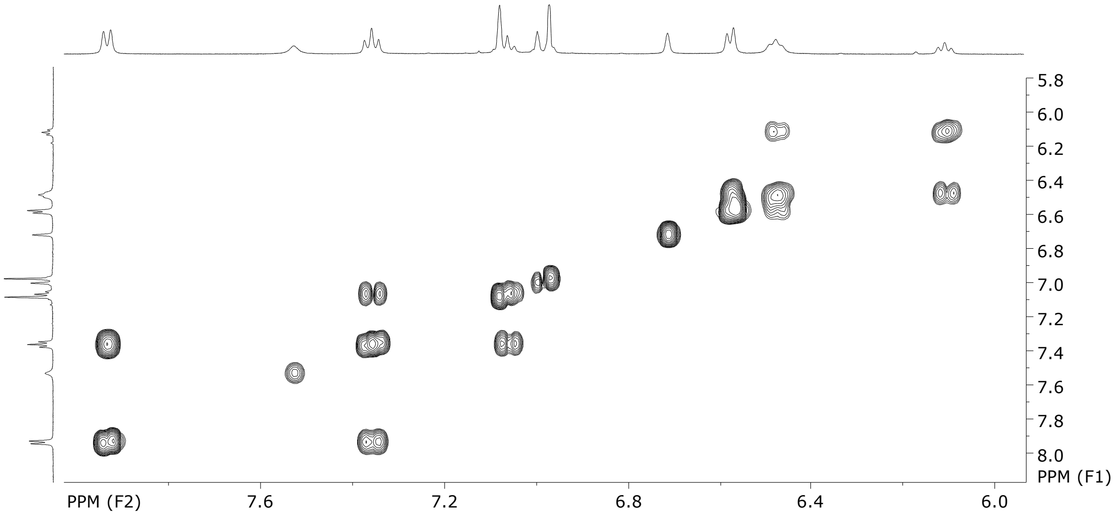

Figure 15. Section of the 2D gCOSY spectrum of Rh[3] in toluene-d_8 at 500 MHz and 60^{o} C, showing all resonances from the six phenyl rings.

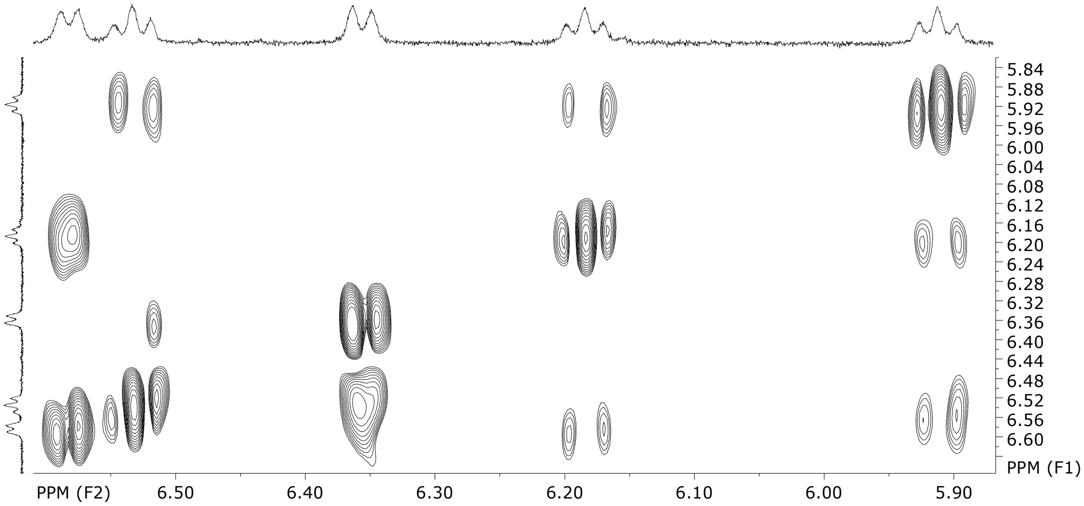

Figure 16. Section of the 2D gCOSY spectrum of Rh[3] in toluene-d_8 at 500 MHz and -55° C, showing coupling between the protons of the “up” phenyl ring.

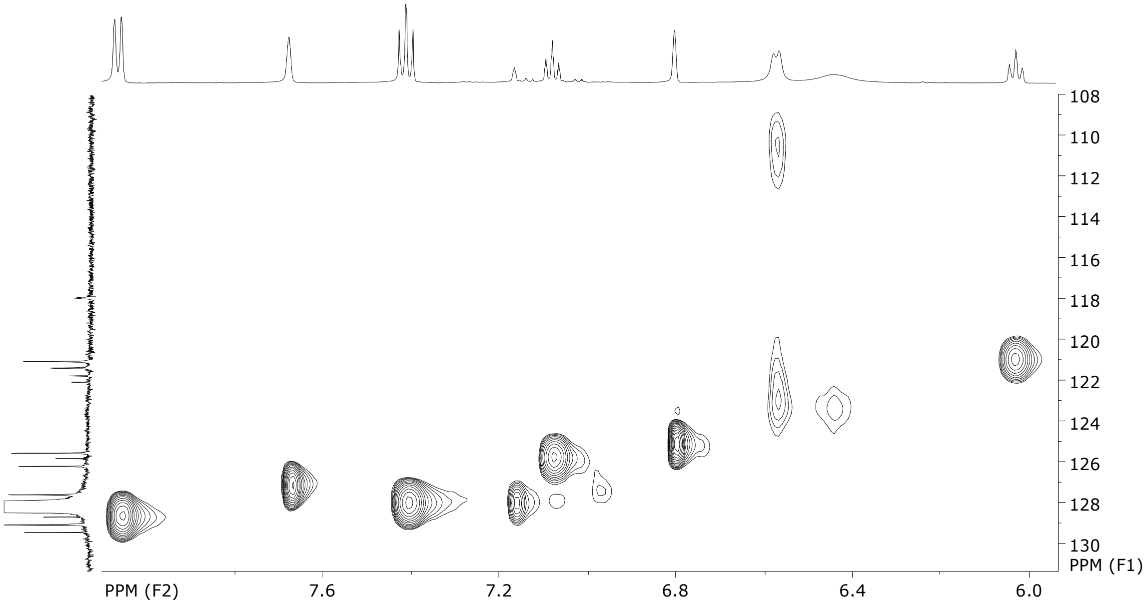

Figure 17. Section of the 2D HMQC spectrum of Rh[**3**], showing the approximate ^{13}C chemical shift of the *ortho* and *meta* carbons of the “up” phenyl rings, though these resonances are too broad to detect in the ^{13}C spectrum itself.

S2 – X-ray diffraction studies

S2.1 General considerations

Diffraction quality crystals for compound [Na(THF)][**2**] was grown from a pentane solution that was chilled to –35 ºC. Yellow prisms of [Na(THF)$_6$][**3**] were obtained by layering Et_2O onto a saturated THF solution at room temperature. Yellow-orange blocks of (THT)Au[**3**], (py)Au[**3**], (py)Ag[**3**], and (py)Cu[**3**], and red blocks of Rh[**3**], were grown via vapor diffusion of pentane into a concentrated THF solution at room temperature. The crystals were mounted inside the glovebox in hydrocarbon oil on a glass fiber. Low-temperature (100K) data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) performing φ- and ω- scans. A semi-empirical absorption correction was applied to the diffraction data using *SADABS*.[4] All structures were solved by direct or Patterson methods using *SHELXS*[5] and refined against F^2 on all data by full-matrix least squares with *SHELXL-97*.[6] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. In structures where disorders were present, the disorders were refined within *SHELXL* with the help of rigid bond restraints as well as similarity restraints on the anisotropic displacement parameters for neighboring atoms and on 1,2 and 1,3 distances throughout the disordered components. The relative occupancies of disordered components were refined freely within *SHELXL*. Details of the data quality and a summary of the residual values of the refinements are listed in Table 1; full structural data is available from the CCDC.[7]

S2.2 Detailed X-ray crystallographic analysis

Compound [Na(THF)][**2**] crystallizes in space group $P2_1/c$. A heavily disordered molecule of pentane is present in the asymmetric unit. The disorder was refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The ratios were refined freely, while constraining the total occupancy of both components to 75%. A slight disorder in two of the three neopentyl groups was handled in a similar fashion. The disorder was refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters. The ratios were refined freely, while constraining the total occupancy of both components to unity.

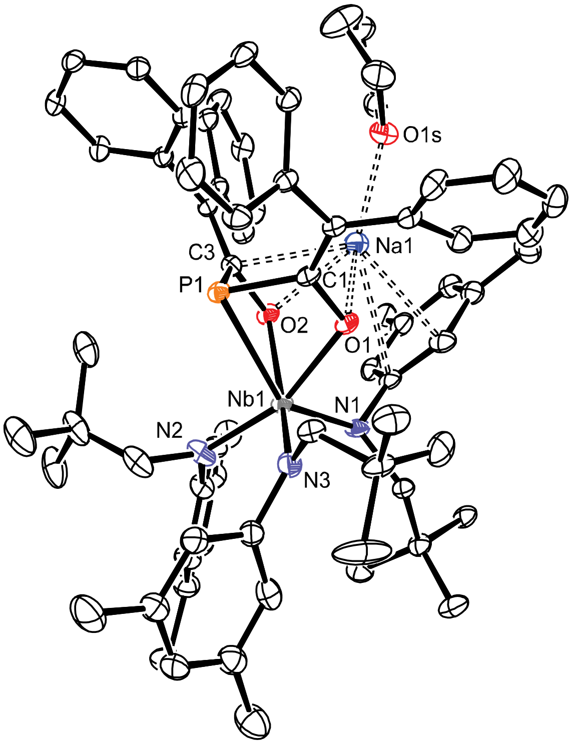

Figure 18. Molecular structure of [Na(THF)][**2**] (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Nb1–N av 2.031(2), Nb1–P1 2.6421(8), Nb–O1 av 2.141(2), P1–C av 1.867(3); N1–Nb1–N2 110.05(11), N2–Nb1–N3 95.11(11), N1–Nb1–N3 109.63(11), C1–P1–C3 94.12(13), C3–P1–Nb1 76.37(9), C1–P1–Nb1 76.17(9).

The asymmetric unit of [Na(THF)$_6$][**3**] contains one third of the molecule together with two Na(THF) fragments, one lying on a special position. One phenyl ring appears disordered over two positions with a ratio of 62:38. The systematic absences in the diffraction data are consistent with the assigned space group of *R*3.

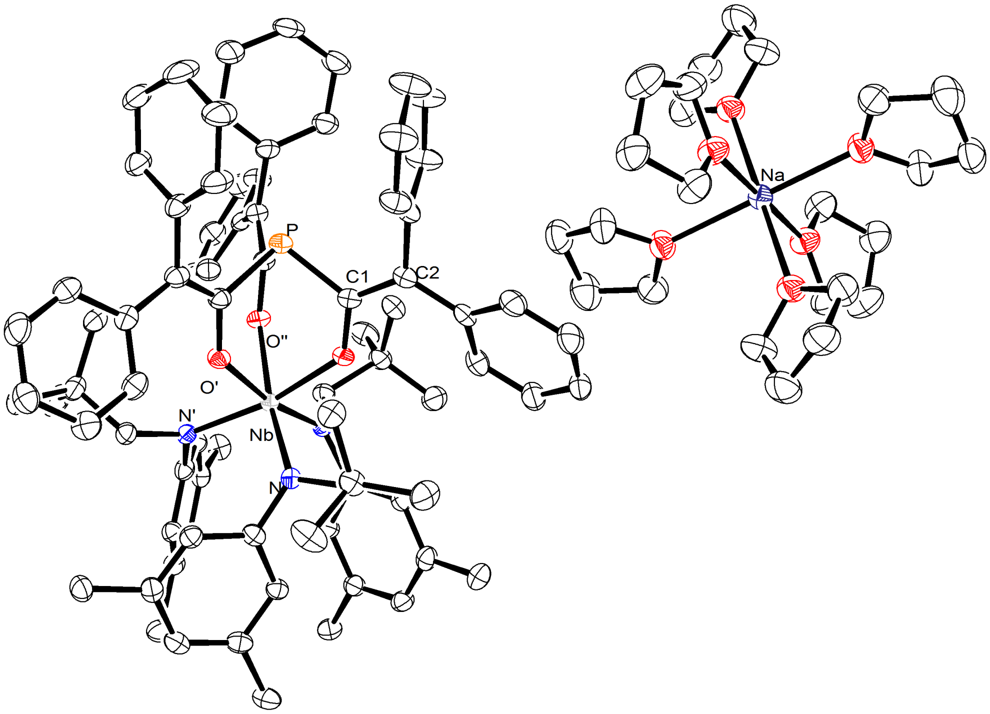

Figure 19. Molecular structure of [Na(THF)$_6$][**3**] (thermal ellipsoids set at 50% probability). The hydrogen atoms are not shown. Atoms marked with a prime are at equivalent positions. Selected bond lengths [Å] and angles [°]: Nb1–N 2.0597(18), Nb1···P1 3.612, Nb1–O1 2.0508(15); N–Nb1–N 97.51(6), C–P1–C 96.49(10).

(THT)Au[**3**] crystallizes in space group $P2_1/c$ with one molecule of (THT)Au[**3**] and 2.5 molecules of THF per asymmetric unit. One THF molecule lies on a special position.

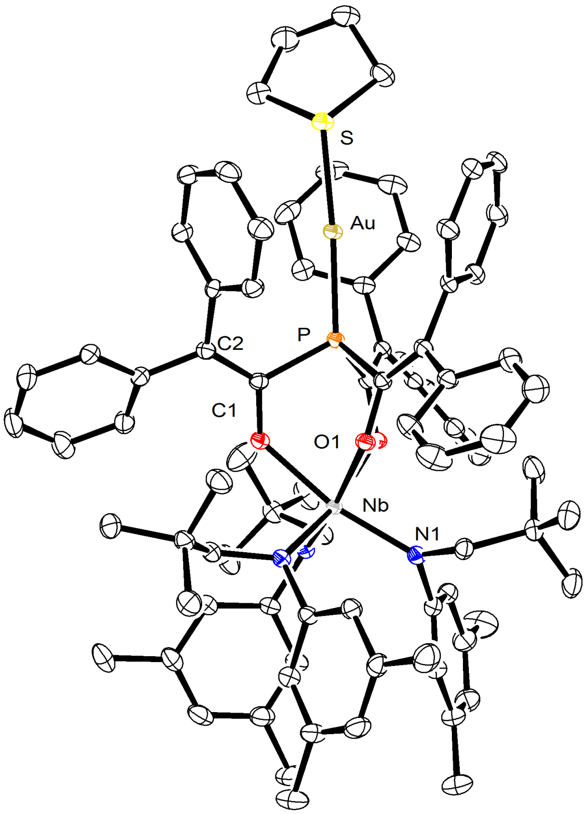

Figure 20. Molecular structure of (THT)Au[**3**] (thermal ellipsoids set at 50% probability). The hydrogen atoms and 2.5 molecules of THF are not shown. Selected bond lengths [Å] and angles [°]: Nb—N1 2.032(3), Nb—O1 2.108(2), P—C1 1.860(3), P—Au 2.2855(8), Au—S 2.3302(9); C1—P—Au 116.56(10), P—Au—S 170.57(3).

(py)Au[**3**] crystallizes in space group $P2_1/c$ with one molecule of (py)Au[**3**] and 2.5 molecules of THF per asymmetric unit. One THF molecule lies on a special position, and each of the other two is disordered over two positions with occupancy factors of 33% and 34% for the minor components.

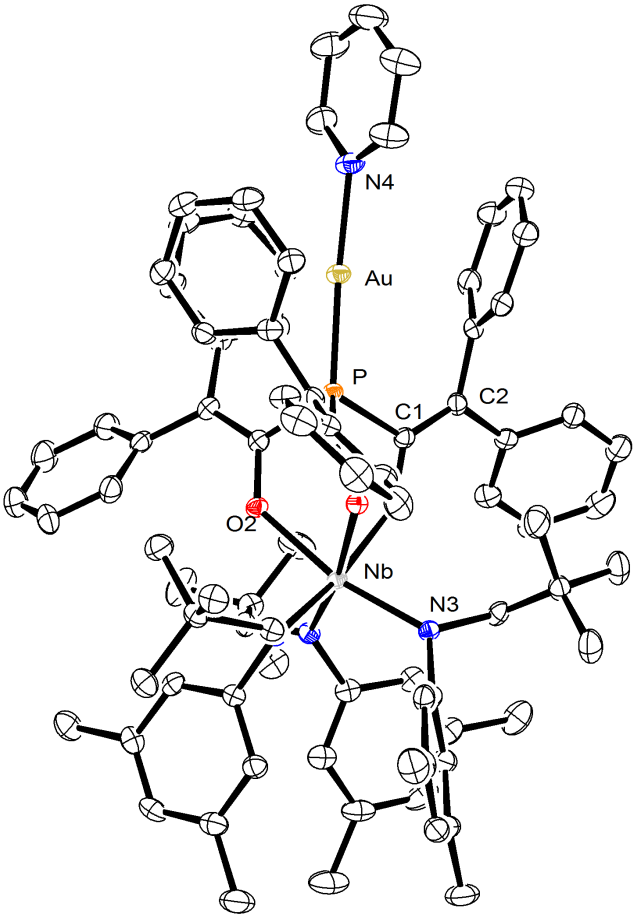

Figure 21. Molecular structure of (py)Au[**3**] (thermal ellipsoids set at 50% probability). The hydrogen atoms and 2.5 molecules of THF are not shown. Selected bond lengths [Å] and angles [°]: Nb—N3 2.031(4), Nb—O2 2.107(4), P—C1 1.850(6), P—Au 2.2466(14), Au—N4 2.092(5); C1—P—Au 115.73(17), P—Au—N4 173.86(15).

(py)Ag[**3**] crystallizes in space group P2$_1$/*c* with one molecule of (py)Ag[**3**] and 2.5 molecules of THF per asymmetric unit. One THF molecule lies on a special position, and each of the other two is disordered over two positions with occupancy factors of 27% and 44% for the minor components.

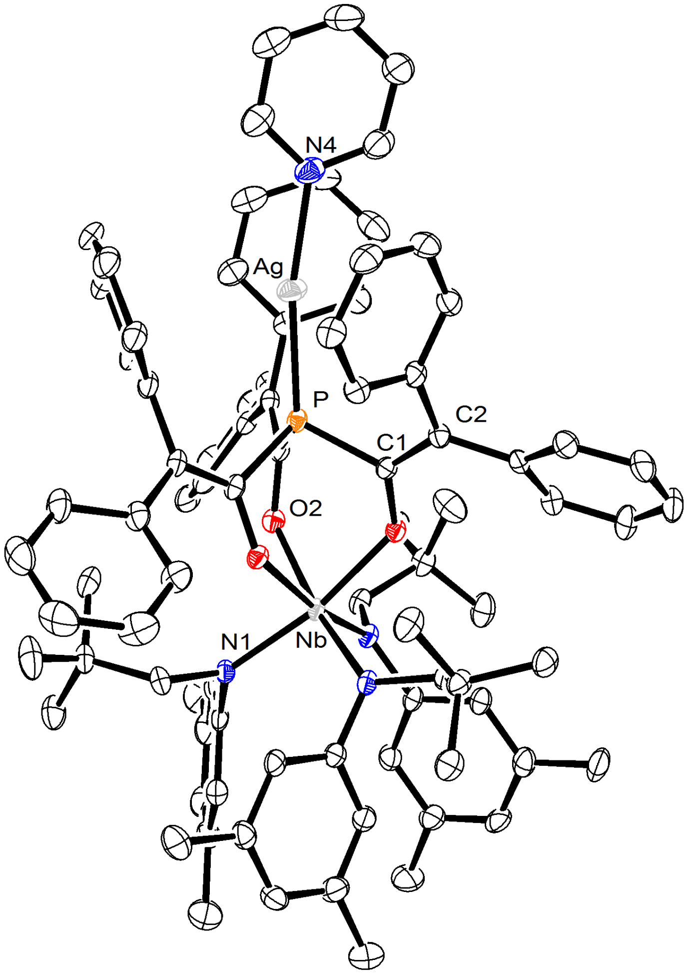

Figure 22. Molecular structure of (py)Ag[**3**] (thermal ellipsoids set at 50% probability). The hydrogen atoms and 2.5 molecules of THF are not shown. Selected bond lengths [Å] and angles [°]: Nb—N3 2.034(2), Nb—O2 2.099(2), P—C1 1.852(3), P—Ag 2.3678(9), Ag—N4 2.162(3); C1—P—Ag 117.19(10), P—Ag—N4 169.13(8).

(py)Cu[**3**] crystallizes in space group $P2_1/c$ with one molecule of (py)Cu[**3**] and 2.5 molecules of THF per asymmetric unit. One THF molecule lies on a special position, and and one of the other two is disordered with an occupancy factor of 41% for the minor component.

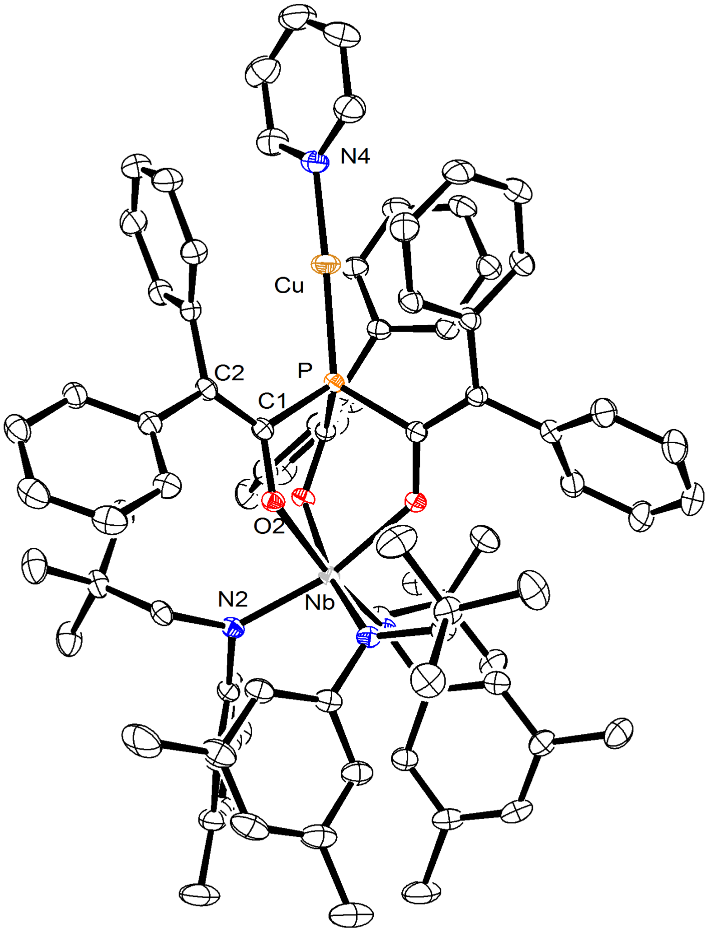

Figure 23. Molecular structure of (py)Cu[**3**] (thermal ellipsoids set at 50% probability). The hydrogen atoms and 2.5 molecules of THF are not shown. Selected bond lengths [Å] and angles [°]: Nb—N3 2.0291(17), Nb—O2 2.0956(15), P—C1 1.844(2), P—Cu 2.1757(6), Cu—N4 1.931(2); C1—P—Cu 115.43(7), P—Cu—N4 172.43(6).

Rh[**3**] crystallizes in space group $P2_1/n$ with one molecule of Rh[**3**] and 2.5 solvent molecules per asymmetric unit. There is one THF molecule on a special position, one THF molecule which is not disordered, and a third solvent site which is disordered between THF (49%) and pentane (51%).

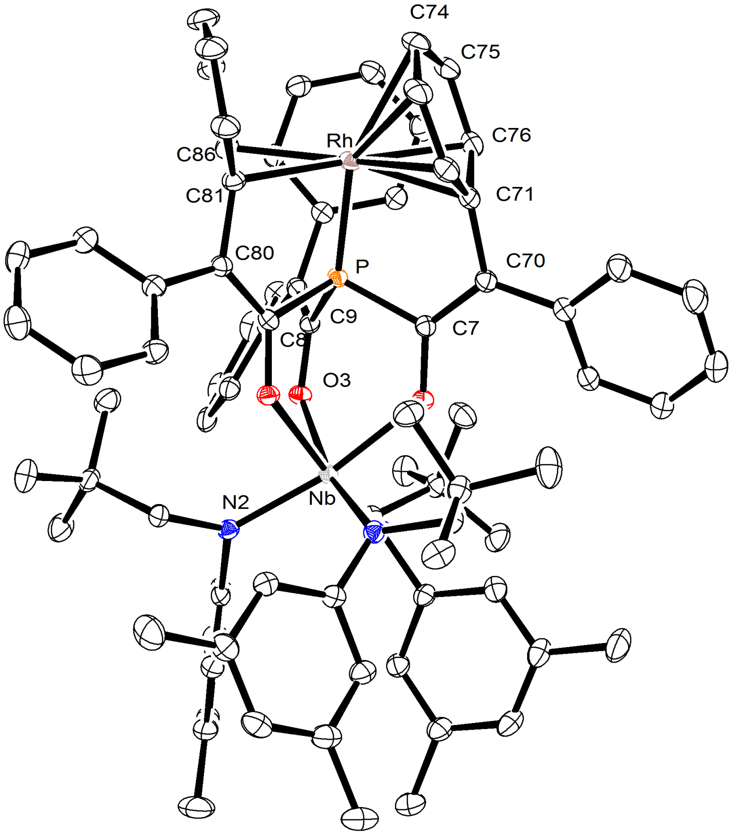

Figure 24. Molecular structure of Rh[**3**] (thermal ellipsoids set at 50% probability). The hydrogen atoms and solvent molecules are not shown. Selected bond lengths [Å] and angles [°]: Nb—N3 2.0260(19), Nb—O2 2.1280(16), P—C7 1.820(2), P—C8 1.824(2), P—C9 1.850(2), P—Rh 2.1643(6), Rh—C81 2.214(2), Rh—C86 2.237(2), Rh—C71 2.195(2), Rh—C72 2.322(2), Rh—C73 2.400(2), Rh—C74 2.415(2), Rh—C75 2.428(2), Rh—C76 2.290(2), C81—C86 1.443, C71—C76 1.439(3), C71—C72 1.432(3), C91—C92 1.398(3), Nb- - -P 3.491; C7—P—Rh 106.48(7), C8—P—Rh 104.31, C9—P—Rh 136.39(7), Nb- - -P—Rh 159.17.

Table 1. Crystallographic data for [Na(THF)][**2**] and [Na(THF)$_6$][**3**].

Compound	**[Na(THF)][2]**	**[Na(THF)$_6$][3]**
Empirical formula	$C_{74.75}H_{97}N_3NaNbO_3P$	$C_{105}H_{138}N_3NaNbO_9P$
Formula weight	1232.42	1733.06
Crystal system	monoclinic	trigonal
Space group	*P*2$_1$/*c* (no. 14)	*R*-3 (no. 148)
a/Å	23.715(2)	17.736(2)
b/Å	16.1639(13)	17.736(2)
c/Å	19.4189(16)	51.913(7)
α/°	90.00	90.00
β/°	107.0020(10)	90.00
γ/°	90.00	120.00
Unit-cell volume/Å^3	7118.4(10)	14143(3)
Z	4	6
μ/mm^{-1}	0.243	0.208
ρ_{calc}/g cm^{-3}	1.150	1.221
T/K	100(2)	100(2)
Crystal size/mm	0.36 × 0.20 × 0.08	0.24 × 0.19 × 0.07
$2\theta_{max}$/°	50.70	56.74
No. of reflections:		
total	13042	7872
unique	10072	5983
No. of parameters	892	416
Residual electron density		
minimum	-0.628	-0.735
maximum	1.009	0.838
$R1$ [$I > 2\sigma(I)$]	0.0455	0.0495
$wR2$ (all data)	0.1310	0.1362
CCDC Number	789474	789473

Table 2. Crystallographic data for (THT)Au[**3**], (py)Au[**3**], (py)Ag[**3**]

Compound	**(THT)Au[3]**	**(py)Au[3]**	**(py)Ag[3]**
Empirical formula	$C_{95}H_{118}N_3NbPO_{5.5}SAu$	$C_{96}H_{115}N_4NbPO_{5.5}Au$	$C_{96}H_{115}N_4NbPO_{5.5}Ag$
Formula weight (g/mol)	1742.83	1733.77	1644.67
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	26.964(4)	27.017(2)	27.086(2)
b/Å	14.145(2)	14.1228(13)	14.0697(11)
c/Å	24.947(4)	24.657(2)	24.790(2)
α/°	90.00	90.00	90.00
β/°	116.938(2)	116.1100(10)	116.3960(10)
γ/°	90.00	90.00	90.00
Unit-cell volume/Å^3	8483(2)	8448.0(13)	8462.3(12)
Z	4	4	4
μ/mm^{-1}	1.960	1.945	0.441
ρ_{calc}/g cm^{-3}	1.365	1.363	1.291
T/K	100(2)	100(2)	100(2)
Crystal size/mm	0.45 x 0.45 x 0.40	0.20 x 0.17 x 0.15	0.45 x 0.40 x 0.35
$2\theta_{max}$/°	59.14	54.20	59.06
No. of reflections:			
total	23816	18630	21967
unique	19101	13842	13833
No. of parameters	1006	993	1077
Residual electron density			
minimum	-1.347	-1.346	-1.094
maximum	2.068	1.731	1.438
R_1 [$I > 2\sigma(I)$]	0.0397	0.0373	0.0523
wR_2 (all data)	0.1032	0.1030	0.1391
CCDC Number	789234	789235	789236

Table 3. Crystallographic data for (py)Cu[**3**], Rh[**3**]

Compound	**(py)Cu[3]**	**Rh[3]**
Empirical formula	$C_{96}H_{115}N_4NbPO_{5.5}Cu$	$C_{91.5}H_{113}N_3NbPO_5Rh$
Formula weight (g/mol)	1600.34	1561.68
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	27.065(3)	23.3525(16)
b/Å	14.0252(16)	15.0941(10)
c/Å	24.972(3)	25.0969(17)
α/°	90.00	90.00
β/°	116.777(2)	115.1470
γ/°	90.00	90.00
Unit-cell volume/$Å^3$	8462.6(17)	8007.8(9)
Z	4	4
μ/mm^{-1}	0.461	0.426
ρ_{calc}/g cm^{-3}	1.256	1.295
T/K	100(2)	100(2)
Crystal size/mm	0.40 x 0.35 x 0.30	0.60 x 0.50 x 0.30
$2\theta_{max}$/°	60.06	60.06
No. of reflections:		
total	24729	23398
unique	19030	18910
No. of parameters	1052	985
Residual electron density		
minimum	-1.392	-0.756
maximum	1.718	1.450
R_1 [$I > 2\sigma(I)$]	0.0471	0.0414
wR_2 (all data)	0.1402	0.1105
CCDC Number	789238	789237

References

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[2] E. C. Taylor, A. McKillop, and G. H. Hawks, *Organic Synthesis*, 1988, **6**, 549.

[3] S. Ahrland, K. Dreisch, B. Noren, and A. Oskarsson, *Mater. Chem. Phys.*, 1993, **35**, 281.

[4] G. M. Sheldrick, *SADABS*; Bruker AXS Inc.: Madison, WI, 2005.

[5] G. M. Sheldrick, *Acta Cryst.,* 1990*,* **A46**, 467.

[6] G. M. Sheldrick. *SHELXL-97, Program for crystal structure determination,* University of Göttingen (Göttingen, Germany, 1997).

[7] The CCDC deposition numbers referenced for each compound in the crystallographic data tables contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif