Versatile Behavior of β-Heterosubstituted Zirconaindene Complexes: M−Cl Bond Activation (M = Si, P, Au Fragments)

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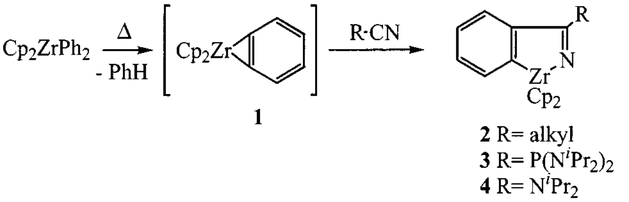
A new way of M–Cl bond activation (M = Si, P, Au fragments) is reported. It consists on the 1,2-addition of M–Cl containing species on the Zr–N bond of azazirconaindene complexes. Unprecedented imino gold complexes incorporating two electron-deficient metallic centers (Au, Zr) have been prepared.

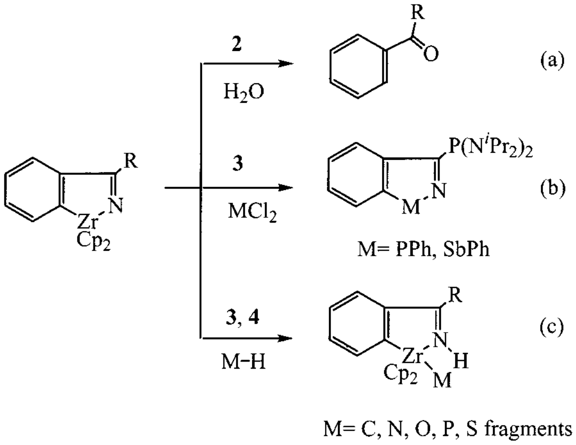
Introduction

The organic and organometallic chemistry of neutral zirconium derivatives is blossoming probably because of the new perspectives zirconium reagents bring in a number of research areas.[1] Among the zirconium synthons generally used, benzyne zirconocene **1** (prepared in situ by photolysis or thermolysis of diphenylzirconocene) is of particular interest because of its high reactivity towards chalcogens, inorganic unsaturated species, alkenes, alkynes, etc.[2] Reactions generally proceed with insertion of the organic or inorganic fragment into Zr−C bonds of the arynezirconocene complex. It is also known that thermolysis of diphenylzirconocene in the presence of nitriles generates azazirconaindenes **2**−**4**,[2,3] (Scheme 1).



Scheme 1. Insertion of nitriles into a Zr−C bond of benzynezirconocene

These metallacycles are versatile tools allowing the development of new strategies of synthesis of useful linear or heterocyclic reagents and ligands. For example, hydrolysis of azazirconaindenes **2** produces ketones in good to excellent yields[2] [Scheme 2, reaction (a)]. Moreover exchange reactions involving **3** and various dihalogenated species allow the preparation of new heterocycles incorporating phosphorus or antimony, and nitrogen[3] [Scheme 2, reaction (b)]. Furthermore, azazirconaindenes act as unusual bases for the deprotonation of several M−H bonds [Scheme 2, reaction (c)]. However the chemical behavior of these complexes depends on the nature of the C-imino substituent. Indeed stable azazirconacyclopentene-substituted phosphanes **3** or amines **4** {R = -P[N(^{i}Pr)$_2$]$_2$, -P[N(Cy)$_2$]$_2$, -N(^{i}Pr)$_2$} when reacted with acetylenic systems, malonitrile derivatives, vinyl acetate, diazo compounds, etc., allow sp^2-, and sp^3-C−H bond activations.[4,5] Similarly, activation of N−H, O−H, P−H, S−H bonds easily occurs in very mild conditions when the same complexes **3**−**4** are treated with aromatic amines, alcohols, phenols, phosphonates or thiols[4] [Scheme 2, reaction (c)].



Scheme 2. Reactivity of β-substituted zirconaindenes

In marked contrast, azazirconaindenes **2** (R = alkyl group) do not react with derivatives incorporating C−H or M−H bonds. Therefore, the basicity of the endocyclic imino nitrogen atom appears to be the driving force in all these M−H bond activations.

The halophilicity of zirconium is also the driving force for many reactions involving zirconium-containing species, but, as illustrated above [Scheme 2, reaction (b)], the reactions generally proceed with Zr−X bond cleavage (X = C, N...) and loss of Cp_2ZrCl_2.

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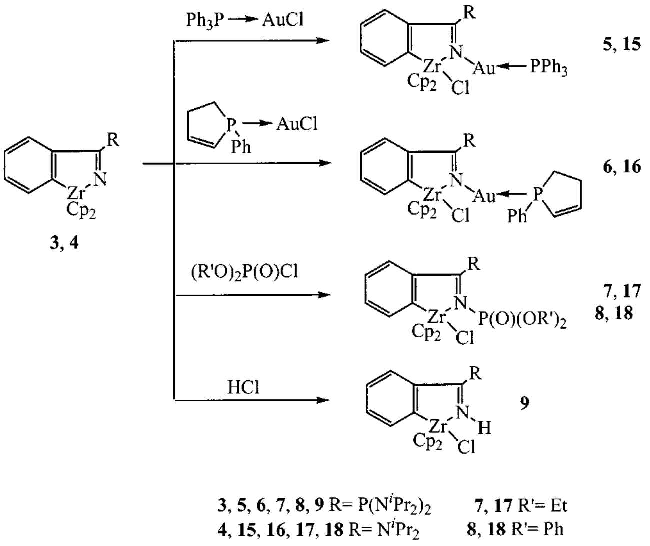
We wish to report here a new facet of the reactivity of azazirconaindene-substituted phosphanes **3** or amines **4**: activation of M−Cl bonds (M = Si, P, Au, H) involving formal 1,2-addition of halogenated compounds to the Zr−N bond of **3** or **4**. These reactions take place without cleavage of the Zr−N and Zr−C bonds, and lead to unprecedented cyclic mono- or bimetallic complexes.

Results and Discussion

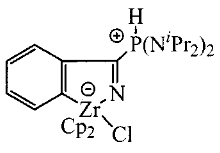
Treatment of the azazirconaindene-substituted phosphane **3** with the gold complex $Ph_3P \rightarrow AuCl$ in THF at 0 °C for 30 min. leads to the formation of the zirconium-gold complex **5** in 73% isolated yield (Scheme 3). The reaction can be monitored by ^{31}P NMR spectroscopy which shows the disappearance of the singlets due to **3** ($\delta = 45.0$) and $Ph_3P \rightarrow AuCl$ ($\delta = 32.5$) and the growth of two doublets at $\delta = 86.0$ $[P(N^iPr_2)_2]$ and $\delta = 44.0$ (Ph_3P) with $^4J_{PP} = 4.5$ Hz. If the same reaction is performed with the phospholene gold complex ($\delta = 40.6$), the azazirconaindene gold complex **6** is formed in 89% yield {$\delta = 86.8$ $[P(N^iPr_2)_2]$ and 52.9 (Ph−P), $^4J_{PP} < 1$ Hz}. ^1H and ^{13}C NMR and IR spectroscopic data are in agreement with the proposed structures for **5** and **6**, which therefore come from a unique 1,2-addition of the Au−Cl bond to the zirconium−nitrogen bond of the starting zirconaindene **3**.

Such a 1,2-addition can be performed with chlorophosphates $(R'O)_2P(O)Cl$. Insertion of the P−Cl bond of diethoxychlorophosphate or diphenoxychlorophosphate takes place at room temperature, leading to the *N*-aminophosphate, C-phosphanyl-disubstituted azazirconaindenes **7** and **8**, respectively. ^{31}P NMR spectroscopy appears to be the tool of choice to establish the structure of **7** and **8**. Two doublets {**7:** $\delta = 45.4$ $[P(N^iPr_2)_2]$, 42.0 $[(O)P(OEt)_2]$, $J_{PP} = 15.8$ Hz; **8:** $\delta = 45.0$ $[P(N^iPr_2)_2]$, 50.3 $[(O)P(OPh)_2]$, $J_{PP} = 17.1$ Hz} were detected strongly suggesting the formation of the $(N^iPr_2)_2P{-}C{=}N{-}P(O)(OEt)_2$ and $(N^iPr_2)_2P{-}C{=}N{-}P(O)(OPh)_2$ imino fragments, respectively.



Scheme 3. 1,2-Addition of halogenated compounds to the Zr−N bond of β-heterosubstituted zirconaindenes

A similar 1,2-addition can be observed when hydrogen chloride (1 M diethyl ether solution) is added to a toluene solution of **3**. The 18-electron zirconium complex **9** is formed as the unique product of the reaction and was isolated in 92% yield after workup. Monitoring the reaction by ^{31}P and ^1H NMR spectroscopy did not show any intermediate or by-product such as, for example, the zwitterion **10**, which might be generated by protonation of the phosphanyl group. It should be noted that a complex similar to **9** was formed, along with other unidentified products, during an unexpected intramolecular alkylation involving the reaction of the benzyne zirconocene **1** with $Br(CH_2)_3CN$.[2]



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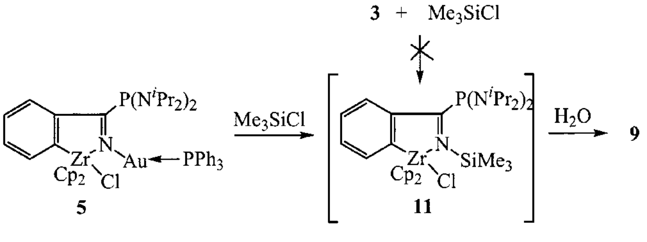
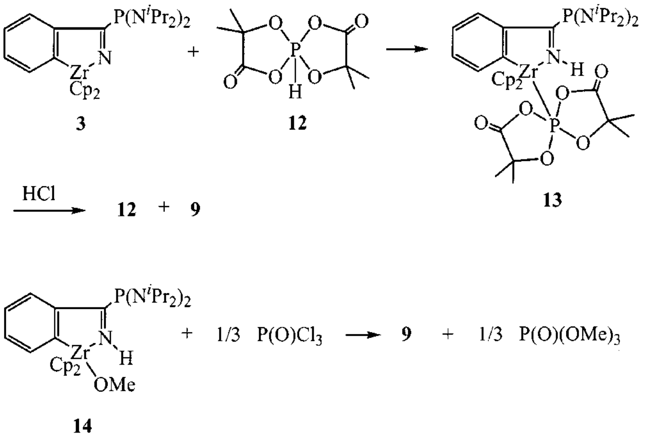
Interestingly, complex **9** can be also formed by different strategies: i) cleavage of the N−M bond (M = Au, P fragments) of the 18-electron azazirconaindenes **5** or **7**, or ii) cleavage of the Zr−M bond (M = P, O) of the zirconaindenes **13** and **14**.

The first strategy (Scheme 4) can be illustrated as follows: addition of chlorotrimethylsilane to the gold complex **5** leads to the formation of $Ph_3P \rightarrow AuCl$ and to the unstable azazirconaindene **11** ($\delta^{31}P = 61$) which, during workup, is transformed into the corresponding NH derivative **9**. It is noteworthy that Si−Cl bond activation is not observed when the 16-electron zirconaindene **3** is reacted directly with chlorotrimethylsilane: no traces of complex **11** (or **9**) are detected in this case.



Scheme 4. Reactivity of the β-phosphanyl-substituted zirconaindene **5**

The second strategy implies the direct cleavage of Zr−M bonds with hydrogen chloride or with halogenated phosphane oxide. A phosphoranide-chloride anion exchange with $Zr{-}P^V$ bond cleavage is observed when the still unique, stable zirconaspirophosphorane **13** (prepared in high yield from the oxidative addition of the P−H spirophosphorane **12** to the azazirconaindene **3**), is treated with hydrogen chloride: the spirophosphorane **12** and the complex **9** (Scheme 5) are the only phosphorus species which can be detected by ^{31}P NMR spectroscopy.



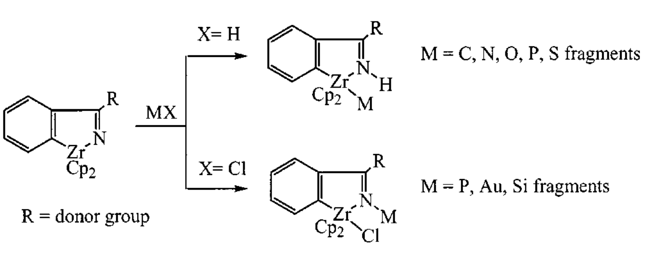
Scheme 5. Synthesis of the β-phosphanyl-substituted zirconaindene **9**

Similarly, the Zr−O bond of the complex **14**,[4] obtained by adding methanol to **3**, can be easily cleaved with trichlorophosphane oxide. The use of 1/3 equiv. of $P(O)Cl_3$ per equivalent of **14** allows us to form **9** and trimethoxyphosphane oxide quantitatively (Scheme 5).

Therefore the 16 electron azazirconaindene-substituted phosphane **3** easily reacts with a variety of halogenated species and is an useful starting reagent for the formation of a number of 18-electron N- and C-disubstituted azazirconaindenes. The corresponding amine **4** presents the same chemical behavior towards gold(I) chloride and chlorophosphates. Thus, complexes **15**−**18** were isolated and fully characterized (Scheme 3).

Conclusion

The versatile behavior of zirconaindene complexes was fully demonstrated. If all the reactions involving these derivatives proceed by a formal 1,2-addition of M−H or M−X reagents to the Zr−N intracyclic bond, the manner of the addition differs dramatically from M−X to M−H species: metallation or phosphorylation at the imino nitrogen atom occurs when halogenated reagents are reacted with zirconaindenes, while protonation takes place with P−H spirophosphorane (Scheme 6). Protonation at nitrogen is also observed with hydrogen chloride. To the best of our knowledge, the gold complexes **5**, **6**, **15**, **16** are the first examples of *N*-imino gold complexes incorporating two electron-deficient metallic centers (Au, Zr). Studies aimed at the generalization of the reactions depicted in Scheme 1 and concerning the use of all these new complexes in organic synthesis is under active investigation.



Scheme 6. Versatile behavior of the β-heterosubstituted zirconaindene towards MX (X = Cl, H) derivatives

Experimental Section

General: All reactions were carried out in the absence of air, under argon, using standard Schlenk techniques and vacuum-line manipulations. All solvents were dried, degassed and distilled before use. A Perkin−Elmer 1725X spectrometer was used for FT-IR. NMR spectra were recorded on Bruker AC80, AC200, or AM250 spectrometers for ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, with $SiMe_4$ (^{1}H, ^{13}C) and H_3PO_4 (^{31}P) as references. The assignment of the ^{13}C NMR signals was done using Jmod, two dimensional HMBC and HMQC, broad band or CW ^{31}P decoupling experiments when necessary.

Compound 5: To a solution of **3** (0.232 g, 0.418 mmol) in THF (5 mL) at room temperature was added triphenylphosphanegold(I) chloride (0.207 g, 0.418 mmol solution in 5 mL of THF). The mixture was stirred at room temperature for 15 min. and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatiles were removed from the solution to give **5** as a yellow solid in 73% yield (0.321 g). − IR (KBr): $\tilde{\nu}$ = 1579 cm^{-1} ($\nu_{C=N}$). − ^{1}H NMR (CD_2Cl_2): δ = 0.98 (d, J_{HH} = 6.0 Hz, 6 H, CH_3), 1.12 (d, J_{HH} = 6.0 Hz, 6 H, CH_3), 1.22 (d, J_{HH} = 5.9 Hz, 6 H, CH_3), 1.32 (d, J_{HH} = 5.9 Hz, 3 H, CH_3), 1.36 (d, J_{HH} = 6.0 Hz, 3 H, CH_3), 3.35 (sept, J_{HH} = 6.1 Hz, 4 H, NCH), 6.00 (s, 10 H, CH_{Cp}), 7.02−7.66 (m, 19 H, CH_{arom}). − ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 24.5 (d, J_{CP} = 5.5 Hz, CH_3), 25.0 (d, J_{CP} = 5.3 Hz, CH_3), 49.1 (d, J_{CP} = 11.4 Hz, NCH), 49.3 (d, J_{CP} = 12.9 Hz, NCH), 49.7 (d, J_{CP} = 11.9 Hz, NCH), 110.9 (s, CH_{Cp}), 124.9 (s, CH_{arom}), 125.8 (d, J_{CP} = 4.4 Hz, CH_{arom}), 126.7 (d, J_{CP} = 5.9 Hz, CH_{arom}), 128.9 (d, J_{CP} = 10.3 Hz, CH_{arom}), 131.0 (s, CH_{arom}), 131.7 (d, J_{CP} = 48.4 Hz, i-Ph), 133.9 (d, J_{CP} = 16.5 Hz, CH_{arom}), 134.4 (d, J_{CP} = 13.8 Hz, CH_{arom}), 139.3 (d, J_{CP} = 7.8 Hz, CH_{arom}), 154.0 (d, J_{CP} = 29.7 Hz, ZrC*C*), 168.8 (d, J_{CP} = 20.0 Hz, ZrC), 198.9 (d, J_{CP} = 3.1 Hz, J_{CP} = 13.2 Hz, PC=N). − ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 44.0 (d, J_{PP} = 5.8 Hz, PPh_3), 86.0 [d, J_{PP} = 5.8 Hz, (iPr$_2$N)$_2$P]. − $C_{47}H_{57}AuClN_3P_2Zr$ (1049.57): calcd. C 53.78, H 5.47; found C 53.89, H 5.54.

Compound 6: To a solution of **3** (0.270 g, 0.486 mmol) in THF (7 mL) at 0 °C was added dihydrophospholegold (I) chloride (0.191 g, 0.486 mmol, solution in 5 mL of THF). The mixture was stirred at room temperature for 0.5 h and then evaporated to dryness. The resulting solid residue was extracted with pentane and filtered. The volatiles were removed from the solution to give **6** as a yellow-brown solid in 89% yield (0.410 g). − IR (KBr): $\tilde{\nu}$ = 1572 cm^{-1} ($\nu_{C=N}$). − ^{1}H NMR (CD_2Cl_2): 0.80−1.52 (m, 24 H, CH_3), 2.34 (m, 1 H, CH_2), 2.92 (m, 2 H, CH_2), 3.28 (m, 4 H, NCH), 3.68 (m, 1 H, CH_2), 5.98 (s, 5 H, CH_{Cp}), 6.00 (s, 5 H, CH_{Cp}), 6.83 (m, 1 H, CH=CH), 7.10 (m, 1 H, CH=CH), 7.11−7.90 (m, 9 H, CH_{arom}),. − ^{13}C{^{1}H} (CD_2Cl_2): δ = 24.6 (d, J_{CP} = 5.4 Hz, CH_3), 25.1 (d, J_{CP} = 5.7 Hz, CH_3), 27.0 (d, J_{CP} = 32.6 Hz, CH_2), 33.8 (s, PCH_2), 49.7 (d, J_{CP} = 10.8 Hz, NCH), 110.8 (s, CH_{Cp}), 124.5 (s, CH_{arom}), 124.7 (d, J_{CP} = 40.4 Hz, CH_{arom}), 125.8 (s, CH_{arom}), 126.4 (d, J_{CP} = 5.8 Hz, CH_{arom}), 128.8 (d, J_{CP} = 9.9 Hz, CH_{arom}), 131.1 (s, CH_{arom}), 132.9 (d, J_{CP} = 13.9 Hz, CH_{arom}), 139.1 (d, J_{CP} = 8.4 Hz, CH_{arom}), 148.9 (d, J_{CP} = 8.7 Hz, CH_{arom}), 154.4 (d, J_{CP} = 22.8 Hz, ZrCC), 168.8 (d, J_{CP} = 18.0 Hz, ZrC), 198.0 (dd, J_{CP} = 4.1 Hz, J_{CP} = 11.3 Hz, PC=N). − ^{31}P{^{1}H} (CD_2Cl_2): δ = 52.9 (Au−P), 86.8 [(iPr$_2$N)$_2$P]. − $C_{39}H_{53}AuClN_3P_2Zr$ (949.45): calcd. C 49.34, H 5.63; found C 49.47, H 5.68.

Compound 7: To a solution of **3** (0.262 g, 0.472 mmol) in toluene (5 mL) at room temperature was added chlorodiethylphosphate (0.091 mL, 0.472 mmol). The mixture was stirred at room temperature for 12 h and then evaporated to dryness. The resulting solid residue was extracted with pentane/toluene (5:1, 20 mL) and filtered. The volatiles were removed from the solution to give **7** as a yellow solid in 72% yield (0.342 g). − IR (KBr): $\tilde{\nu}$ = 1579 cm^{-1} ($\nu_{C=N}$), 1247 ($\nu_{P=O}$). − ^{1}H NMR (C_6D_6): δ = 1.09 (t, J_{HH} = 7.1 Hz, 6 H, OCH$_2$CH_3), 1.20 (d, J_{HH} = 6.6 Hz, 12 H, CH$_3$), 1.23 (d, J_{HH} = 6.6 Hz, 12 H, CH$_3$), 3.48 (sept, J_{HH} = 6.6 Hz, 4 H, NCH), 3.94 (dq, J_{HH} = 7.1 Hz, 2 H, OCH_2CH$_3$), 4.12 (dq, J_{HH} = 7.1 Hz, 2 H, OCH_2CH$_3$), 6.11 (s, 10 H, CH$_{Cp}$), 6.89−7.11 (m, 3 H, CH$_{arom}$), 7.55−8.03 (m, 1 *H*, CH$_{arom}$). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 17.2 (d, J_{CP} = 4.7 Hz, OCH$_2$CH_3), 24.5 (d, J_{CP} = 5.3 Hz, CH$_3$), 24.7 (d, J_{CP} = 6.0 Hz, CH$_3$), 48.9 (d, J_{CP} = 11.1 Hz, NCH), 62.8 (d, J_{CP} = 6.1 Hz, OCH$_2$CH$_3$), 114.7 (s, CH$_{Cp}$), 125.4 (dd, J_{CP} = 10.1 Hz, J_{CP} = 17.2 Hz, CH$_{arom}$), 128.4 (d, J_{CP} = 11.1 Hz, CH$_{arom}$), 131.4 (d, J_{CP} = 10.5 Hz, CH$_{arom}$), 132.4 (d, J_{CP} = 2.5 Hz, CH$_{arom}$), 142.7 (dd, J_{CP} = 36.1 Hz, J_{CP} = 50.7 Hz, ZrCC), 192.1 (dd, J_{CP} = 11.3 Hz, J_{CP} = 19.9 Hz, ZrC), 202.4 (d, J_{CP} = 33.9 Hz, PC=N). − ^{31}P{^{1}H} (C_6D_6): δ = 42.0 (d, J_{PP} = 15.8 Hz, P=O), 45.4 [d, J_{PP} = 15.8 Hz, (iPr$_2$N)$_2$P]. − $C_{33}H_{52}ClN_3O_3P_2Zr$ (727.41): calcd. C 54.49, H 7.21; found C 54.60, H 7.28.

Compound 8: To a solution of **3** (0.281 g, 0.506 mmol) in toluene (5 mL) at room temperature was added chlorodiphenylphosphate (0.105 mL, 0.506 mmol). The mixture was stirred at room temperature for 12 h and then evaporated to dryness. The resulting solid residue was extracted with pentane/toluene (5:1, 20 mL) and filtered. The volatiles were removed from the solution to give **8** as a yellow solid in 75% yield (0.313 g). − IR (KBr): $\tilde{\nu}$ = 1188 cm^{-1} ($\nu_{P\text{-}O}$), 1259 ($\nu_{P=O}$), 1587 (C=N). − ^{1}H NMR (CD_2Cl_2): δ = 1.22 (d, J_{HH} = 5.7 Hz, 12 H, CH$_3$); 1.29 (d, J_{HH} = 6.5 Hz, 12 H, CH$_3$), 3.28 (m, 2 H, NCH), 3.52 (m, 2 H, NCH), 6.37 (s, 5 H, CH$_{Cp}$), 6.42 (s, 5 H, CH$_{Cp}$), 6.61−7.25 (m, 12 H, CH$_{arom}$), 7.80 (m, 1 H, CH$_{arom}$), 8.04 (m, 1 H, CH$_{arom}$). − ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 24.4 (d, J_{CP} = 5.3 Hz, CH$_3$), 49.1 (d, J_{CP} = 10.4 Hz, NCH), 50.1 (d, J_{CP} = 10.4 Hz, NCH), 114.9 (s, CH$_{Cp}$), 118.6 (s, CH$_{arom}$), 120.5 (d, J_{CP} = 4.4 Hz, CH$_{arom}$), 121.6 (d, J_{CP} = 3.0 Hz, CH$_{arom}$), 125.9 (d, J_{CP} = 27.8 Hz, CH$_{arom}$), 128.6 (d, J_{CP} = 10.5 Hz, CH$_{arom}$), 129.9 (d, J_{CP} = 11.8 Hz, CH$_{arom}$), 130.4 (s, CH$_{arom}$), 132.0 (d, J_{CP} = 10.6 Hz, CH$_{arom}$), 133.4 (s, CH$_{arom}$), 142.7 (dd, J_{CP} = 33.3 Hz, J_{CP} = 52.3 Hz, ZrCC), 150.9 (d, J_{CP} = 8.12 Hz, i-OPh), 165.9 (d, J_{CP} = 14.5 Hz, ZrC), 196.1 (dd, J_{CP} = 11.5 Hz, J_{CP} = 20.5 Hz, PC=N). − ^{31}P{^{1}H} (CD_2Cl_2): δ = 45.0 [d, J_{PP} = 17.0 Hz, (iPr$_2$N)$_2$P], 50.3 [d, J_{PP} = 17.0 Hz, P=O)]. − $C_{41}H_{52}ClN_3O_3P_2Zr$ (823.50): calcd. C 59.80, H 6.36; found C 59.95, H 6.42.

Compound 9: To a solution of **3** (0.201 g, 0.362 mmol) in toluene (5 mL) at −78 °C was added hydrogen chloride (1 M solution in diethyl ether; 0.362 mL). The mixture was stirred for 15 min. at this temperature. The resulting solution was then stirred at room temperature for 15 min. leading to the formation of **9** in quantitative yield as monitored by ^{31}P{^{1}H} NMR spectroscopy. The resulting solid residue was extracted with pentane (15 mL) and filtered to give **9**[5] as a yellow solid in 92% yield (0.197 g). − IR (KBr): $\tilde{\nu}$ = 1576 cm^{-1} ($\nu_{C=N}$), 3305 ($\nu_{N\text{-}H}$). − ^{1}H NMR (C_6D_6): δ = 1.11 (d, J_{HH} = 6.6 Hz, 12 H, CH$_3$), 1.21 (d, J_{HH} = 6.6 Hz, 12 H, CH$_3$), 3.27 (sept., J_{HH} = 6.6 Hz, 4 H, CH), 5.9 (s, 10 H, CH$_{Cp}$), 7.20 (m, 2 H, CH$_{arom}$), 7.88 (m, 1 H, CH$_{arom}$), 8.25 (m, 1 H, CH$_{arom}$), 10.12 (d, J_{HP} = 5.02 Hz, 1 H, NH). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 24.4 (d, J_{CP} = 6.8 Hz, CH$_3$), 25.1 (d, J_{CP} = 5.0 Hz, CH$_3$), 49.6 (d, J_{CP} = 11.2 Hz, CH), 111.3 (s, C$_p$), 128.8 (s, CH$_{arom}$), 129.8 (s, CH$_{arom}$), 130.1 (d, J_{CP} = 14.3 Hz, CH$_{arom}$), 141.2 (s, CH$_{arom}$), 146.1 (d, J_{CP} = 24.1 Hz, C$_{arom}$), 198.6 (d, J_{CP} = 6.3 Hz, C$_{arom}$), 202.5 (d, J_{CP} = 40.6 Hz, PC=N). − ^{31}P{^{1}H} NMR (C_6D_6): δ = 58.2. − $C_{29}H_{43}ClN_3PZr$ (823.50): calcd. C 58.90, H 7.33; found C 59.06, H 7.37.

Compound 13: To a solution of **3** (0.212 g, 0.382 mmol) in toluene (5 mL) at room temperature was added tetraoxispirophosphorane (0.071 g, 0.382 mmol). The mixture was stirred at room temperature for 15 min. and then evaporated to dryness. The resulting solid residue was extracted with pentane (15 mL) and filtered. The volatiles were removed from the solution to give **13** as a yellow solid in 88% yield (0.249 g). − IR (KBr): $\tilde{\nu}$ = 1153 cm^{-1} ($\nu_{C\text{-}O}$), 1551 ($\nu_{C=N}$), 1657 ($\nu_{C=O}$). − ^{1}H NMR (CD_2Cl_2): δ = 0.98 (d, J_{HH} = 6.6 Hz, 3 H, CH$_3$), 1.14 (d, J_{HH} = 6.6 Hz, 3 H, CH$_3$), 1.16 (d, J_{HH} = 6.6 Hz, 3 H, CH$_3$), 1.21 (d, J_{HH} = 6.7 Hz, 3 H, CH$_3$), 1.23 (d, J_{HH} = 6.6 Hz, 3 H, CH$_3$), 1.24 (d, J_{HH} = 6.7 Hz, 3 H, CH$_3$), 1.30 (d, J_{HH} = 6.7 Hz, 6 H, CH$_3$), 1.60 [d, J_{HP} = 1.6 Hz, 12 H, C(CH$_3$)$_2$], 3.42 (m, 4 H, NCH), 5.97 (s, 5 H, CH$_{Cp}$), 5.98 (s, 5 H, CH$_{Cp}$), 7.21 (m, 2 H, CH$_{arom}$), 7.80 (m, 1 H, CH$_{arom}$), 8.15 (dd, J_{HH} = 6.9 Hz, J_{HP} = 3.25 Hz, 1 H, CH$_{arom}$), 9.60 (d, J_{HP} = 4.9 Hz, 1 H, C=N−H). − ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 23.8 (d, J_{CP} = 5.6 Hz, CH$_3$), 23.9 (d, J_{CP} = 5.6 Hz, CH$_3$), 24.2 (d, J_{CP} = 5.6 Hz, CH$_3$), 24.5 (d, J_{CP} = 5.6 Hz, CH$_3$), 24.6 (d, J_{CP} = 5.1 Hz, CH$_3$), 26.7 [d, J_{CP} = 4.3 Hz, C(CH_3)$_2$], 28.1 [d, J_{CP} = 4.3 Hz, C(CH_3)$_2$], 48.8 (d, J_{CP} = 11.6 Hz, NCH), 49.0 (d, J_{CP} = 11.6 Hz, NCH), 76.2 [d, J_{CP} = 7.4 Hz, C(CH$_3$)$_2$], 110.8 (s, CH$_{Cp}$), 122.5 (s, CH$_{arom}$), 129.3 (s, CH$_{arom}$), 129.5 (d, J_{CP} = 14.3 Hz, CH$_{arom}$), 140.2 (s, CH$_{arom}$), 145.2 (d, J_{CP} = 26.1 Hz, ZrCC), 177.9 (d, J_{CP} = 7.2 Hz, C=O), 197.3 (d, J_{CP} = 6.0 Hz, ZrC), 204.6 (d, J_{CP} = 41.2 Hz, PC=N). − ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 55.7 {s, P[N(iPr)$_2$]$_2$}, 128.2 (s, ZrP).

Compound 15: To a solution of **4** (0.250 g, 0.558 mmol) in THF (5 mL) at room temperature was added triphenylphosphanegold(I) chloride (0.277 g, 0.558 mmol, solution in 5 mL of THF). The mixture was stirred at room temperature for 12 h and then evaporated to dryness. The resulting solid residue was extracted with CH$_2$Cl$_2$/pentane (1:10, 20 mL) and filtered. The volatiles were removed from the solution to give **15** as a yellow solid in 82% yield (0.432 g). − IR (KBr): $\tilde{\nu}$ = 1597 cm^{-1} ($\nu_{C=N}$). − ^{1}H NMR (CD_2Cl_2): δ = 1.10 (d, J_{HH} = 6.7 Hz, 3 H, CH$_3$), 1.12 (d, J_{HH} = 6.7 Hz, 3 H, CH$_3$), 1.35 (d, J_{HH} = 6.7 Hz, 3 H, CH$_3$), 1.41 (d, J_{HH} = 6.7 Hz, 3 H, CH$_3$), 3.43 (m, 2 H, NCH), 6.32 (s, 10 H, CH$_{Cp}$), 7.15−7.81 (m, 19 H, CH$_{arom}$). − ^{13}C NMR (CD_2Cl_2): δ = 18.4 (s, CH$_3$), 18.8 (s, CH$_3$), 47.7 (s, NCH), 114.2 (s, CH$_{Cp}$), 124.6 (s, CH$_{arom}$), 125.8 (d, J_{CP} = 15.2 Hz, CH$_{arom}$), 127.4 (s, CH$_{arom}$), 128.6 (d, J_{CP} = 12.2 Hz, CH$_{arom}$), 129.1 (d, J_{CP} = 10.2 Hz, CH$_{arom}$), 131.4 (s, CH$_{arom}$), 132.0 (d, J_{CP} = 10.1 Hz, CH$_{arom}$), 134.3 (d, J_{CP} = 14.0 Hz, CH$_{arom}$), 139.9 (d, J_{CP} = 28.3 Hz, CH$_{arom}$), 141.2 (s, ZrCC), 166.3 (s, ZrC), 194.7 (s, NC=N). − ^{31}P{^{1}H} (CD_2Cl_2): δ = 45.2. − $C_{41}H_{43}AuClN_2PZr$ (918.42): calcd. C 53.62, H 4.72; found C 53.69, H 4.81.

Compound 16: To a solution of **4** (0.248 g, 0.554 mmol) in THF (5 mL) at 0 °C was added dihydrophospholegold (I) chloride (0.230, 0.584 mmol, solution in 5 mL of THF). The mixture was stirred at room temperature for 2 h and then evaporated to dryness. The resulting solid residue was washed with diethyl ether (3 mL) and filtered to give **16** as a white powder in 92% yield (0.440 g.). − IR (KBr): $\tilde{\nu}$ = 1578 cm^{-1} ($\nu_{C=N}$). − ^{1}H NMR (CD_2Cl_2): δ = 0.80−1.72 (m, 12 H, CH$_3$), 2.22 (m, 1 H, CH$_2$), 2.62 (m, 2 H, CH$_2$), 2.95 (m, 2 H, NCH), 3.89 (m, 1 H, CH$_2$), 6.31 (s, 5 H, CH$_{Cp}$), 6.33 (s, 5 H, CH$_{CP}$), 6.87 (m, 1 H, CH=CH), 7.10 (m, 1 H, CH=CH), 7.12−7.92 (m, 9 H, CH_{arom}). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 20.1 (s, CH_3), 20.3 (s, CH_3), 26.4 (d, J_{CP} = 34.4 Hz, CH_2), 33.8 (s, PCH_2), 45.4 (s, NCH), 110.8 (s, CH_{Cp}), 124.4 (d, J_{CP} = 29.4 Hz, CH_{arom}), 125.3 (s, CH_{arom}), 127.4 (s, CH_{arom}), 129.1 (d, J_{CP} = 10.4 Hz, CH_{arom}), 131.5 (s, CH_{arom}), 132.9 (d, J_{CP} = 13.7 Hz, CH_{arom}), 139.6 (d, J_{CP} = 19.3 Hz, CH_{arom}), 150.9 (s, ZrC*C*), 167.9 (d, J_{CP} = 13.3 Hz, ZrC), 201.0 (s, NC=N). − $^{31}P\{^1H\}$ (CD_2Cl_2): δ = 57.3. − $C_{33}H_{39}AuClN_2PZr$ (818.30): calcd. C 48.44, H 4.80; found C 48.57, H 4.96.

Compound 17: To a solution of **4** (0.314 g, 0.739 mmol) in toluene (7 mL) at room temperature was added chlorodiethylphosphate (0.097 mL, 0.739 mmol). The mixture was stirred at room temperature for 3 h and then evaporated to dryness. The resulting solid residue was extracted with CH_2Cl_2/pentane (1:8, 15 mL) and filtered. The volatiles were removed from the solution to give **17** as a yellow solid in 75% yield (0.331 g.). − IR (KBr): $\tilde{\nu}$ = 1583 cm^{-1} ($\nu_{C=N}$). 1232 ($\nu_{P=O}$). − ^1H NMR (CD_2Cl_2): δ = 1.07 (d, J_{HH} = 6.8 Hz, 3 H, CH_3), 1.22 (t, J_{HH} = 7.1 Hz, 6 H, OCH_2CH_3), 1.23 (d, J_{HH} = 6.8 Hz, 3 H, CH_3), 1.40 (d, J_{HH} = 6.8 Hz, 3 H, CH_3), 1.61 (d, J_{HH} = 6.8 Hz, 3 H, CH_3), 3.15 (m, 2 H, NCH), 4.07 (dq, J = 7.1 Hz, 4 H, OCH_2CH_3), 6.31 (s, 10 H, CH_{Cp}), 7.18−7.91 (m, 4 H, CH_{arom}). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 16.3 (d, J_{CP} = 6.0 Hz, OCH_2CH_3), 20.6 (s, CH_3), 49.3 (s, NCH), 61.6 (d, J_{CP} = 5.9 Hz, OCH_2CH_3), 114.1 (s, CH_{Cp}), 124.1 (s, CH_{arom}), 127.7 (s, CH_{arom}), 131.0 (s, CH_{arom}), 131.5 (s, CH_{arom}), 138.7 (d, J_{CP} = 33.3 Hz, ZrC*C*), 164.3 (d, J_{CP} = 19.6 Hz, ZrC), 193.2 (s, NC=N). − $^{31}P\{^1H\}$ (CD_2Cl_2): δ = 42.1. − $C_{41}H_{52}ClN_3O_3P_2Zr$ (596.26): calcd. C 54.39, H 6.42; found 54.56, H 6.55.

Compound 18: To a solution of **4** (0.290 g, 0.683 mmol) in toluene (8 mL) at room temperature was added chlorodiphenylphosphate (0.141 mL, 0.683 mmol). The mixture was stirred at room temperature for 15 min. and then evaporated to dryness. The resulting solid residue was extracted with pentane/toluene (5: 1, 20 mL) and filtered. The volatiles were removed from the solution to give **18** as a beige solid in 65% yield (0.307 g). − IR (KBr): $\tilde{\nu}$ = 1198 cm^{-1} ($\nu_{P=O}$) 1286 ($\nu_{P\text{-}OPh}$), 1588 ($\nu_{C=N}$). − ^1H NMR ([D_8]toluene): δ = 0.98 (d, J_{HH} = 6.5 Hz, 12 H, CH_3), 2.54 (sept, J_{HH} = 6.5 Hz, 2 H, NCH), 5.92 (s, 5 H, CH_{Cp}), 6.02 (s, 5 H, CH_{Cp}), 6.64−7.52 (m, 14 H, CH_{arom}). − $^{13}C\{^1H\}$ NMR ([D_8]toluene): 21.8 (s, CH_3), 22.3 (s, CH_3), 50.3 (s, NCH), 51.8 (s, NCH), 113.2 (s, CH_{Cp}), 115.4 (s, CH_{Cp}), 119.1, 121.3, 128.2, 129.6, 130.7 (s, CH_{arom}), 166.9 (s, ZrC*C*), 180.6 (s, ZrC), 198.3 (s, NC=N). − $^{31}P\{^1H\}$ ([D_8]toluene): δ = 40.6.

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