(202.3 MHz, CDCl$_3$): $\delta = 116.96$; ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 8.48$ (br, 1H), 7.54 (d, 1H, $J_{4,5} = 7.5$ Hz), 7.51 (d, 1H, $J_{6,7} = 7.5$ Hz), 7.45 (s, 1H), 7.19–7.35 (m, 7H), 6.12 (m, 1H), 4.90 (m, 1H), 4.36 (m, 1H), 3.45–4.00 (m, 8H), 3.50 (m, 3H), 3.26 (m, 1H), 3.13 (m, 1H), 2.96 (m, 1H), 2.23 (m, 1H), 2.01–2.06 (m, 1H), 1.82–1.95 (m, 7H), 0.91 (s, 9H), 0.08 (2s); HRMS (FAB): calcd for $C_{40}H_{53}N_5O_7PSi$: 774.3452; found: 774.3455.

15: DBU (37 µL, 0.25 mmol) was added to a stirred solution of **12** (38.6 mg, 0.05 mmol) and 3'-*O*-TBDMS-thymidine (35.6 mg, 0.1 mmol) in dry THF (2 mL) at room temperature. After 20 min, the ^{31}P NMR spectrum of the reaction mixture showed a single signal at around $\delta = 140$. The mixture was then loaded onto a short column to filter off DBU. After evaporation of the solvent, the residue was dissolved in dry CH$_2$Cl$_2$, and Beaucage's reagent (10 mg, 0.05 mmol) was added at room temperature. After stirring for 5 min, ^{31}P NMR spectroscopy revealed a single peak at around $\delta = 68$. The solvent was removed, the residue was dissolved in THF, and TBAF was added. After 2 h, the solvent was removed in vacuo. CH$_2$Cl$_2$ was added to the residue, and the extract was washed with water and brine and dried over magnesium sulfate. Purification by column chromatography afforded **15** as a white solid (28 mg, 61 %).

16 and **17**: Phosphorothioate **15** (28 mg, 0.026 mmol) was dissolved in concentrated ammonia/ethanol (3/1, 5 mL). The mixture was heated at 55 °C for 16 h. The ^{31}P NMR signal shifted quantitatively from $\delta = 68$ to 56. The reaction mixture was extracted with chloroform several times. The combined organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed to provide **17** (9.2 mg, 91 %) as a light yellow solid. The aqueous crude product was purified by flash chromatography to give **16** (15 mg, 89 %).

17: ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 7.41$ (d, 1H, $J = 8.0$ Hz), 7.23–7.35 (m, 6H), 7.13 (m, 1H), 7.02 (m, 1H), 4.71 (br, 1H), 4.04–4.14 (m, 2H), 3.94 (m, 2H), 3.68–3.86 (m, 2H), 3.11–3.23 (m, 4H), 2.97 (m, 1H), 2.82 (m, 1H), 1.55–1.82 (m, 5H); HRMS (FAB): calcd for $C_{24}H_{29}N_4O$: 389.2341 $[(M+1)]^+$; found: 389.2343.

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Early Transition Metal α-Diazoalkane Complexes[**]

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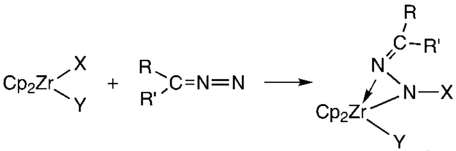
The reaction of diazoalkanes with transition metals results either in coordination through the nitrogen atoms or in formation of a carbon–metal bond. Many N-bonded substituted transition metal diazoalkanes have been studied,[1] but only four series of C-bonded late transition metal compounds have been isolated.[2] α-Metalated diazoalkanes L$_n$M–C(N$_2$)R containing an early transition metal have not yet been reported. Treatment of zirconocene Zr^{IV} complexes with diazoalkanes results in insertion into Zr–C,[3] Zr–H,[3c] Zr–P,[4] and zirconium–metal bonds[5] to give the corresponding hydrazonato ligands **I** [Eq. (1)].



I

(1)

We have shown that 1-aza-zirconacyclopentene complexes **1a** and **1b**[6] (see Scheme 1) contain a strongly electrophilic metal center (mostly because of the inductive electron-withdrawing properties of the σ-bonded nitrogen atom) and a rather nucleophilic imido group that does not share its lone-pair electron density with the adjacent metal center because of the strain in the metallacycle.[7] Indeed phosphanes **1a** and **1b** activate C–H bonds in relatively acidic carbonic acids, such as acetylenes and methylene compounds.[8] Although electrophilic, metal-mediated, aliphatic C–H bond cleavage is precedented,[9] its application to the functionalization of complex substrates is very rare. The present report deals with a novel electrophilic sp^2-C–H bond activation and its application for the preparation of α-diazomethylzirconium complexes, which are the first C-metalated diazoalkanes L$_n$MC(N$_2$)R with an early transition metal.

Treatment of **1a** and **1b** with ethyl diazoacetate (**2**) in THF at room temperature gave the light yellow, thermally stable solids **4a** and **4b** (Scheme 1) in excellent yields (>88 %). The ^{31}P NMR spectra of **4a** and **4b** display a singlet at $\delta = 49.4$ and 58.5, respectively. The total disappearance of the sp^2-CH

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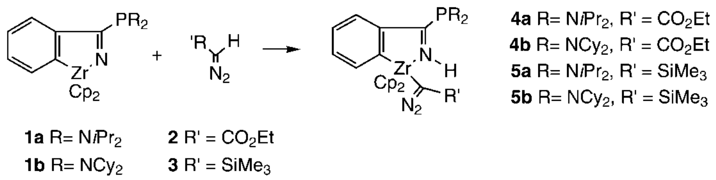


Scheme 1. Synthesis of α-diazomethyl zirconium complexes **4a**, **b** and **5a**, **b**.

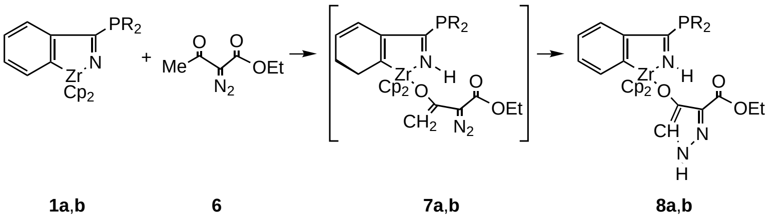
chemical shift of the starting reagent **2** was monitored by ^{1}H NMR spectroscopy, which showed the presence of a broad, low-field signal for the NH proton at $\delta = 9.55$ and 9.74 in the final products **4a** and **4b**, respectively. In addition to the chemical shifts corresponding to the aza-zirconocene metallacycle skeleton (the resonances for the Cp groups appear as one singlet), the ^{1}H and ^{13}C NMR spectra exhibited signals in the region expected for the CO_2Et ester group bonded to the diazo functionality. The most striking data of the C-coordinated $C(N_2)$ diazo group in **4a** and **4b** are the ^{13}C NMR chemical shifts at $\delta = 48.1$ and 47.0,[2, 10] respectively, and the intense band at 2029 cm^{-1} in the IR spectra for C=N=N, which is shifted to lower frequency in comparison with that of the starting diazoalkanes.[2] All these data are fully in accordance with the structure proposed for **4a** and **4b**.

An identical experimental procedure was conducted with trimethylsilyldiazomethane (**3**) and **1a**, **b** to prepare the corresponding C-α-metalated diazoalkane complexes **5a** and **5b**, which were isolated in good yield (Scheme 1). The ^{1}H and ^{13}C NMR spectra exhibited the expected chemical shifts for the $SiMe_3$ fragment and showed signals at $\delta = 30.5$ (**5a**) and 36.7 (**5b**) for the Zr−C(N_2) carbon atom.[2, 10] The IR spectra displayed a characteristic band at 2069 (**5a**) and 2049 cm^{-1} (**5b**) for the diazo C=N=N group. Thus spectroscopic and analytical data[11] are consistent with the formulation of **4a**, **b** and **5a**, **b** as the first α-C-zirconated diazoalkanes.

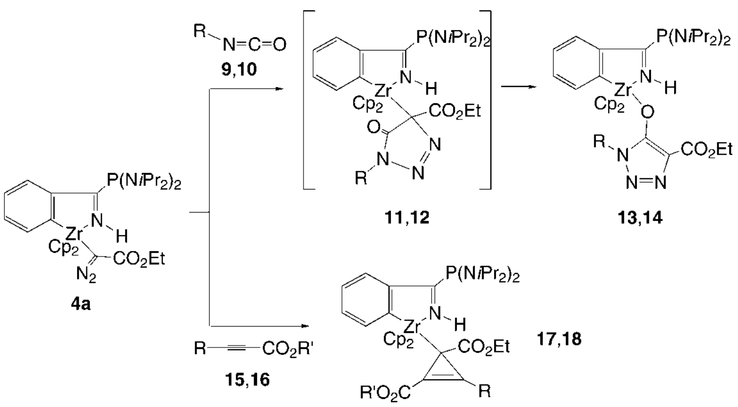
Interestingly when **1a** and **1b** were allowed to react with the "nonterminal" diazo compound **6**, the pyrazoles **8a** and **8b** were obtained in good yield (Scheme 2). These new compounds were unambiguously characterized by mass spectrometry as well as by IR and NMR spectroscopy (see the Experimental Section). Formation of the metalated heterocycles **8a** and **8b** could be rationalized by O−H bond activation of the enol tautomer of substrate **6**, leading to the zirconocene diazo intermediates **7a** and **7b**, which rearrange by an intramolecular [3+2] cycloaddition to give the isolated products **8a** and **8b**.

In a first approach, the reactivity of the C-α-metalated diazoalkane complex **4a** was tested by addition of phenyl isocyanate (**9**) to afford the 1,2,3-triazolato zirconocene enolate complex **13** (Scheme 3). As evidenced from ^{31}P, ^{1}H, and ^{13}C NMR spectroscopies, the structure of the aza-zirconocene metallacycle skeleton remained unchanged. In particular, the ^{1}H NMR signal of the NH group appeared as expected at $\delta = 9.59$ and the ^{13}C NMR shift for P−C=N was observed at $\delta = 201.3$ with $J_{C,P} = 38.5$ Hz (**4a**: $\delta(^{13}C) = 203.9$, $J_{C,P} = 39.3$ Hz). No IR absorption corresponding to a diazo group was identified in **13**. In the ^{13}C NMR spectrum the signals corresponding to the triazole skeleton at $\delta = 119$ and 162 are in the range usually observed for sp^2 carbon atoms bonded to ester and ether groups, respectively.

An identical reaction was conducted with naphtyl isocyanate (**10**) and **4a** (Scheme 3). The isolated triazole **14**[11] exhibited the same spectroscopic data as **13**. However, to characterize unambiguously the cycloaddition products **13** and **14**, a single-crystal X-ray analysis of **14** was undertaken (Figure 1, see the Experimental Section). The features at the



Scheme 2. Reactions of the enolizable diazo compound **6** with **1a**, **b**. **a**: R = N*i*Pr$_2$, **b**: R = NCy$_2$.



Scheme 3. Cycloaddition reactions of the α-diazomethyl zirconium complex **4a**. **9**, **11**, **13**: R = Ph; **10**, **12**, **14**: R = α-Naph; **15**, **17**: R = CO_2Et, R' = Et; **16**, **18**: R = H, R' = Me.

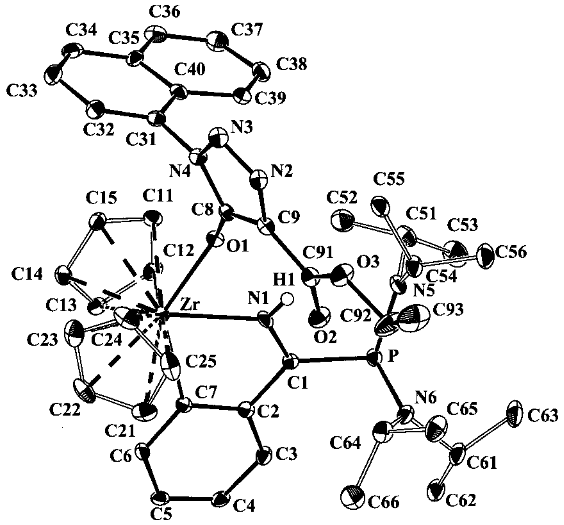
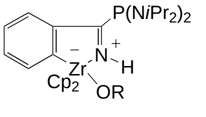


Figure 1. ZORTEP drawing of the molecular structure of **14**. Selected bond lengths [Å] and angles [°]: Zr-O1 2.220(4), Zr-N1 2.258(4), Zr-C7 2.390(4), N1-C1 1.281(5), C1-P 1.861(4); O1-Zr-N1 70.89(12), N1-Zr-C7 67.71(13), Zr-O1-C8 146.1(2), Zr-N1-C1 126.1(3), Zr-C7-C2 116.3(3).

Cp_2Zr unit are typical for bent metallocene complexes.[12] The atoms of the aza-zirconacyclopentene skeleton are practically coplanar and lie roughly in the equatorial plane which bisects the dihedral angle formed by the Cp ligands. The bond lengths and angles in the five-membered heterocycle are typical for 1*H*-1,2,3-triazolato compounds.[13] The large C7-Zr1-O1 angle of 138.07(11)° and the short Zr1–N1 bond length of 2.258(4) Å, which is halfway between those of typical neutral Cp_2Zr^{IV}–N σ bonds (≈2.20 Å) and Cp_2Zr^{IV}–N π-type interactions (≈2.40 Å), are the truly outstanding structural features in **14**.[14] Therefore this product could formally be represented as the iminium–zirconate complex **II**.[15]



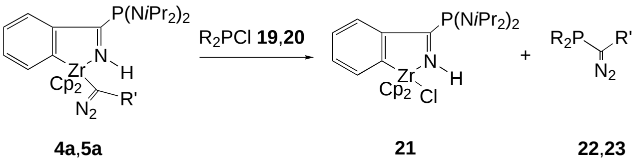
II

It is reasonable to propose in a first step a [3+2] dipolar cycloaddition[16] of the diazo function in **4a** with the isocyanate group in **9** and **10** with transient formation of **11** and **12** (Scheme 3). Then due to the high oxophilicity of the zirconium atom and the resulting aromaticity of the five-membered ring in the final product, an intramolecular rearrangement occurs to give the metalonate triazole complexes **13** and **14**. Formation of enolate complexes by transformation of acyl zirconocene compounds has been reported;[17] however, in the case where the carbonyl group is located in the *β*-position with respect to the metal, this rearrangement is unprecedented.

Diazo compounds are classical precursors of carbenes. It is well known that transition metal complexes catalyze the decomposition of diazoacetates in the presence of acetylenes.[18] Addition of **4a** to the acetylene dicarboxylate **15** resulted in loss of nitrogen and formation of the stable C-metalated cyclopropene compound **17**,[11] which was isolated in 96% yield (Scheme 3). The intense $\nu(C(N_2))$ absorption at 2029 cm^{-1} for **4a** totally disappeared, while characteristic bands for **17** at 1566 (C=N), 1725 (CO), and 3335 cm^{-1} (NH) were observed. The ^1H and ^{13}C chemical shifts of the aza-zirconocene metallacycle skeleton in **17** appeared in the expected range (^1H NMR: $\delta(NH) = 10.64$; ^{13}C NMR: $\delta(P{-}C{=}N) = 202.0$, $J_{C,P} = 38.5$ Hz). The cyclopropene ring in **17** exhibited, beside the chemical shift of the corresponding CO_2Et ester groups, two singlets at $\delta = 118.7$ (sp^2-C) and 146.1 (Zr–C).

The terminal acetylenic compound **16** reacted with **4a** to give the corresponding cyclopropene complex **18** as the unique product (Scheme 3); no C/H insertion was observed.[18] In the ^1H NMR spectrum the resonance for the imino =NH group was identified at $\delta = 11.22$, and the signal at $\delta = 7.79$ was unambiguously assigned to the =CH group of the three-membered ring.[19] The $^{13}C\{^1H\}$ NMR spectrum showed three singlets at $\delta = 117.3$ (=CH), 144.7, and 145.3 (ZrC and sp^2-C) for the cyclopropene ring.[19] We can propose, for the first time, that the loss of nitrogen from **4a** in the formation of the cyclopropene rings **17** and **18** is initiated by the presence of the zirconium metal fragment.

Organometallocene Group 4 complexes are useful intermediates in organic synthesis since various procedures for the cleavage of carbon–zirconium bonds with electrophiles have been reported.[20] Addition of chlorodiphenylphosphane (**19**) to **4a** resulted in transfer of the diazo $C(N_2)R'$ moiety to the phosphorus atom to give, as the unique products, **21** and the *α*-diazophosphane **22** (^{31}P NMR: $\delta = -21$; Scheme 4). However **22** decomposed by intermolecular reactions of the diazo moiety with the lone pair on phosphorus.[21] Then **5a** was treated with **20** to provide the stable diazo compound **23**[22] along with the metal complex **21**.



Scheme 4. Reactions of the *α*-diazomethyl zirconium complexes **4a** and **5a** with chlorophosphanes **19** and **20**. **19**, **22**: R = Ph, R′ = CO_2Et; **20**, **23**: R = N*i*Pr_2, R′ = $SiMe_3$.

In summary we have prepared by an unprecedented sp^2-C–H bond activation the first stable *α*-C-zirconated diazoalkanes **4a**,**b** and **5a**,**b**. The reactions of **4a** with isocyanates and acetylenic derivatives showed the large versatility of these species to give metallacycle compounds (**13**/**14**, **17**/**18**) without or with the loss of nitrogen. In future work the thermal and photochemical behavior of the C-metalated zirconocene diazo complexes will be examined.

Experimental Section

Synthetic procedures and spectroscopic data for compounds **13**, **14**, and **21** can be found in the Supporting Information.

4a, **b**: Ethyl diazoacetate (**2**; 0.048 mL, 0.465 mmol for **4a**; 0.063 mL, 0.599 mmol for **4b**) was added at room temperature to a solution of **1a** (0.258 g, 0.465 mmol) or **1b** (0.428 g, 0.599 mmol) in toluene (5 mL). The mixture was stirred at room temperature for 10 min (30 min for **4b**) and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatile components were removed from the solution to give the product.

4a: Yellow solid, 0.283 g (91% yield). IR (KBr): $\tilde{\nu} = 1571$ ν(C=N), 1661 ν(C=O), 2029 ν(C=N=N), 3375 cm^{-1} ν(N–H); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta =$ 49.4 (s); ^1H NMR (C_6D_6): $\delta = 1.09$ (d, $J_{H,H} = 6.5$ Hz, 12H; CH_3), 1.16 (t, $J_{H,H} = 7.0$ Hz, 3H; OCH_2CH_3), 1.19 (d, $J_{H,H} = 5.9$ Hz, 12H; CH_3), 3.46 (m, 4H; NCH), 4.14 (q, $J_{H,H} = 7.0$ Hz, 2H; CH_2), 5.75 (s, 10H; CH_{Cp}), 7.00–7.18 (m, 2H; CH_{arom}), 7.47 (d, $J_{H,H} = 7.3$ Hz, 1H; CH_{arom}), 8.30 (m, 1H; CH_{arom}), 9.55 (d, $J_{H,P} = 5.3$ Hz, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 15.5$ (s; OCH_2CH_3), 24.4 (d, $J_{C,P} = 6.1$ Hz; CH_3), 24.8 (d, $J_{C,P} = 5.5$ Hz; CH_3), 48.1 (s; C=N=N), 49.2 (d, $J_{C,P} = 11.6$ Hz; NCH), 59.8 (s; CH_2), 109.6 (s; CH_{Cp}), 123.3, 129.5, 142.3 (s; CH_{arom}), 129.7 (d, $J_{C,P} = 21.0$ Hz; CH_{arom}), 146.3 (d, $J_{C,P} = 27.6$ Hz; ZrC*C*), 174.7 (s; C=O), 196.9 (d, $J_{C,P} = 6.9$ Hz; ZrC), 203.9 (d, $J_{C,P} = 39.3$ Hz; PC=N); elemental analysis calcd for $C_{33}H_{48}N_5O_2PZr$ (668.96) (%): C 59.25, H 7.23, N 10.47; found: C 59.23, H 7.29, N 10.51.

4b: Yellow solid, 0.437 g (88% yield). IR (KBr): $\tilde{\nu} = 1571$ ν(C=N), 1661 ν(C=O), 2029 ν(C=N=N), 3355 cm^{-1} ν(N–H); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta =$ 58.5 (s); ^1H NMR (C_6D_6): $\delta = 0.83$–1.89 (m, 40H; CH_2), 1.21 (t, $J_{H,H} =$ 7.1 Hz, 3H; OCH_2CH_3), 3.13 (m, 4H; NCH), 4.23 (q, $J_{H,H} = 7.1$ Hz, 2H; OCH_2), 5.85 (s, 10H; CH_{Cp}), 7.08–7.20 (m, 2H; CH_{arom}), 7.52 (d, $J_{H,H} =$ 8.0 Hz, 1H; CH_{arom}), 8.50 (m, 1H; CH_{arom}), 9.74 (d, $J_{H,P} = 5.5$ Hz, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 15.4$ (s; OCH_2CH_3), 26.3, 27.1 (s; CH_2), 35.5 (d, $J_{C,P} = 6.1$ Hz; CH_2), 36.1 (d, $J_{C,P} = 4.2$ Hz; CH_2), 47.0 (s; C=N=N), 58.8 (d, $J_{C,P} = 9.8$ Hz; NCH), 59.9 (s; OCH_2), 109.6 (s; CH_{Cp}), 123.4, 129.3, 142.1 (s; CH_{arom}), 130.1 (d, $J_{C,P} = 19.3$ Hz; CH_{arom}), 146.7 (d, $J_{C,P} = 28.2$ Hz; ZrC*C*), 174.5 (s; C=O), 196.9 (d, $J_{C,P} = 6.5$ Hz; ZrC), 204.0 (d, $J_{C,P} = 43.6$ Hz; PC=N); elemental analysis calcd for $C_{45}H_{64}N_5O_2PZr$ (829.23) (%): C 65.18, H 7.77, N 8.44; found: C 65.12, H 7.81, N 8.42.

5a,b: (Trimethylsilyl)diazomethane (**3**, 2.0 M in hexanes; 0.302 mL, 0.604 mmol for **5a**; 0.489 mL, 0.979 mmol for **5b**) was added at room temperature to a solution of **1a** (0.335 g, 0.604 mmol) or **1b** (0.700 g, 0.979 mmol) in toluene (8 mL). The mixture was heated under reflux for 20 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatile components were removed from the solution to give the product.

5a: Yellow solid, 0.287 g (71 % yield). IR (KBr): $\tilde{\nu} = 1571$ ν(C=N), 2069 ν(C=N=N), 3325 cm^{-1} ν(N–H); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 57.2$ (s); ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 0.35$ (s, 9H; SiMe$_3$), 1.11 (d, $J_{\mathrm{H,H}} = 6.6$ Hz, 12H; CH$_3$), 1.18 (d, $J_{\mathrm{H,H}} = 6.6$ Hz, 12H; CH$_3$), 3.25 (m, 4H; NCH), 5.90 (s, 10H; CH$_{\mathrm{Cp}}$), 6.98–7.40 (m, 3H; CH$_{\mathrm{arom}}$), 8.18 (d, $J_{\mathrm{H,H}} = 7.9$ Hz, 1H; CH$_{\mathrm{arom}}$), 9.62 (d, $J_{\mathrm{H,P}} = 5.6$ Hz, 1H; NH); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 2.5$ (s; SiMe$_3$), 24.5 (d, $J_{\mathrm{C,P}} = 7.1$ Hz; CH$_3$), 24.6 (d, $J_{\mathrm{C,P}} = 6.2$ Hz, CH$_3$), 30.5 (s, C=N=N), 49.6 (d, $J_{\mathrm{C,P}} = 10.9$ Hz, NCH), 110.2 (s; CH$_{\mathrm{Cp}}$), 122.7, 129.5, 141.2 (s; CH$_{\mathrm{arom}}$), 129.7 (d, $J_{\mathrm{C,P}} = 12.7$ Hz; CH$_{\mathrm{arom}}$), 146.9 (d, $J_{\mathrm{C,P}} = 23.9$ Hz; ZrC*C*), 198.1 (d, $J_{\mathrm{C,P}} = 6.4$ Hz; ZrC), 202.2 (d, $J_{\mathrm{C,P}} = 37.4$ Hz; PC=N); elemental analysis calcd for $\mathrm{C_{33}H_{52}N_5PSiZr}$ (669.08) (%): C 59.24, H 7.83, N 10.46; found: C 59.19, H 7.79, N 10.51.

5b: Yellow solid, 0.600 g (74 % yield); IR (KBr): $\tilde{\nu} = 1571$ ν(C=N), 2049 ν(C=N=N), 3315 cm^{-1} ν(N–H); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 63.7$ (s); ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 0.35$ (s, 9H; SiMe$_3$), 0.83–2.05 (m, 40H; CH$_2$), 2.91 (m, 4H; NCH), 5.93 (s, 10H; CH$_{\mathrm{Cp}}$), 6.98–7.40 (m, 3H; CH$_{\mathrm{arom}}$), 8.28 (d, $J_{\mathrm{H,H}} = 7.6$ Hz, 1H; CH$_{\mathrm{arom}}$), 9.70 (d, $J_{\mathrm{H,P}} = 5.7$ Hz, 1H; NH); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 2.5$ (s; SiMe$_3$), 26.3, 27.5 (s; CH$_2$), 35.6 (d, $J_{\mathrm{C,P}} = 5.6$ Hz; CH$_2$), 35.9 (br; CH$_2$), 36.7 (s; C=N=N), 59.7 (br; NCH), 110.2 (s; CH$_{\mathrm{Cp}}$), 122.7, 129.4, 141.1 (s; CH$_{\mathrm{arom}}$), 129.8 (d, $J_{\mathrm{C,P}} = 15.6$ Hz; CH$_{\mathrm{arom}}$), 147.1 (d, $J_{\mathrm{C,P}} = 23.8$ Hz; ZrC*C*), 198.2 (d, $J_{\mathrm{C,P}} = 6.2$ Hz; ZrC), 201.9 (d, $J_{\mathrm{C,P}} = 39.2$ Hz; PC=N); elemental analysis calcd for $\mathrm{C_{45}H_{68}N_5PSiZr}$ (829.34) (%): C 65.17, H 8.26, N 8.44; found: C 65.21, H 8.29, N 8.50.

8a,b: Ethyl diazoacetoacetate (**6**; 0.053 mL, 0.388 mmol for **8a**; 0.069 mL, 0.500 mmol for **8b**) was added at room temperature to a solution of **1a** (0.215 g, 0.388 mmol) or **1b** (0.357 g, 0.500 mmol) in toluene (5 mL). The mixture was stirred at room temperature for 1 h and then evaporated to dryness. The resulting solid residue was extracted with pentane (15 mL) and filtered. The volatile components were removed from the solution to give the product.

8a: Yellow solid, 0.242 g (88 % yield). MS (FAB/MNBA): *m/z*: 709 [M^+]; IR (KBr): $\tilde{\nu} = 1551$ ν(C=N), 1591 ν(C=N), 1715 ν(C=O), 3204 ν(N–H), 3355 cm^{-1} ν(N–H); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 51.6$ (s); ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 0.87$ (t, $J_{\mathrm{H,H}} = 7.1$ Hz, 3H; OCH$_2$C*H*$_3$), 1.11 (d, $J_{\mathrm{H,H}} = 6.7$ Hz, 12H; CH$_3$), 1.21 (d, $J_{\mathrm{H,H}} = 6.4$ Hz, 12H; CH$_3$), 3.46 (m, 4H; NCH), 4.16 (q, $J_{\mathrm{H,H}} = 7.1$ Hz, 2H; CH$_2$), 5.96 (s, 10H; CH$_{\mathrm{Cp}}$), 7.04–7.41 (m, 3H; CH$_{\mathrm{arom}}$), 7.46 (s, 1H; =CH), 8.34 (m, 1H; CH$_{\mathrm{arom}}$), 9.82 (d, $J_{\mathrm{H,P}} = 5.3$ Hz, 1H; C=NH), 11.29 (br, 1H; =NNH); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 15.2$ (s; OCH$_2$CH$_3$), 24.5 (d, $J_{\mathrm{C,P}} = 6.0$ Hz; CH$_3$), 24.8 (d, $J_{\mathrm{C,P}} = 5.0$ Hz; CH$_3$), 49.3 (d, $J_{\mathrm{C,P}} = 11.2$ Hz; NCH), 59.6 (s; CH$_2$), 111.2 (s; CH$_{\mathrm{Cp}}$), 122.9, 129.5, 141.3 (s; CH$_{\mathrm{arom}}$), 129.8 (d, $J_{\mathrm{C,P}} = 17.4$ Hz; CH$_{\mathrm{arom}}$), 139.5 (s; =CH), 147.8 (d, $J_{\mathrm{C,P}} = 26.1$ Hz; ZrC*C*), 148.9 (s; C=N), 158.5 (s; =C-O), 160.5 (s; C=O), 198.6 (s; ZrC), 201.3 (d $J_{\mathrm{C,P}} = 38.6$ Hz; PC=N); elemental analysis calcd for $\mathrm{C_{35}H_{50}N_5O_3PZr}$ (711.00) (%): C 59.12, H 7.08, N 9.85; found: C 59.07, H 7.12, N 9.81.

8b: Orange solid, 0.309 g (71 % yield). IR (KBr): $\tilde{\nu} = 1536$ ν(C=N), 1561 ν(C=N), 1725 ν(C=O), 3296 ν(N–H), 3325 cm^{-1} ν(N–H); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 64.0$ (s); ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 0.77$–1.94 (m, 43H; CH$_2$, CH$_3$), 2.97 (m, 4H; NCH), 4.25 (q, $J_{\mathrm{H,H}} = 6.8$ Hz, 2H; OCH$_2$), 6.04 (s, 10H; CH$_{\mathrm{Cp}}$), 6.99–7.24 (m, 2H; CH$_{\mathrm{arom}}$), 7.41 (d, $J_{\mathrm{H,H}} = 6.8$ Hz, 1H; CH$_{\mathrm{arom}}$), 7.47 (s, 1H; =CH), 8.47 (d, $J_{\mathrm{H,H}} = 7.1$ Hz, 1H; CH$_{\mathrm{arom}}$), 9.88 (d, $J_{\mathrm{H,P}} = 5.2$ Hz, 1H; C=NH), 10.54 (br, 1H; =NNH); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 15.2$ (s; CH$_3$), 26.3 (s, CH$_2$), 27.4 (d, $J_{\mathrm{C,P}} = 6.3$ Hz; CH$_2$), 35.6 (br; CH$_2$), 59.5 (br; NCH), 59.7 (s; OCH$_2$), 111.3 (s; CH$_{\mathrm{Cp}}$), 122.7, 129.5, 141.1 (s; CH$_{\mathrm{arom}}$), 130.2 (d, $J_{\mathrm{C,P}} = 13.1$ Hz; CH$_{\mathrm{arom}}$), 139.4 (s; =CH), 147.4 (d, $J_{\mathrm{C,P}} = 24.1$ Hz; ZrC*C*), 147.6 (s; C=N), 157.9 (s; =C-O), 160.6 (s; C=O), 199.0 (d, $J_{\mathrm{C,P}} = 5.0$ Hz; ZrC), 201.6 (d, $J_{\mathrm{C,P}} = 41.3$ Hz; PC=N); elemental analysis calcd for $\mathrm{C_{47}H_{66}N_5O_2PZr}$ (871.26) (%): C 64.79, H 7.63, N 8.03; found: C 64.73, H 7.68, N 8.07.

17 and **18**: Diethyl acetylenedicarboxylate (**15**; 0.049 mL, 0.311 mmol for **17**) or methyl propiolate (**16**; 0.071 mL, 0.803 mmol for **18**) was added at room temperature to a solution of **4a** (0.208 g, 0.311 mmol for **17**; 0.537 g, 0.803 mmol for **18**) in toluene (5 mL). The mixture was stirred at room temperature for 1 h and then evaporated to dryness. The resulting solid residue was extracted with pentane (15 mL) and filtered. The volatile components were removed from the solution to give the product.

17: Yellow solid, 0.242 g (96 % yield). IR (KBr): $\tilde{\nu} = 1566$ ν(C=N), 1725 ν(C=O), 3335 cm^{-1} ν(N–H); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 40.9$ (s); ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 0.94$–1.18 (m, CH$_3$, 27H; OCH$_2$C*H*$_3$), 1.35 (d, $J_{\mathrm{H,H}} = 6.5$ Hz, 6H; CH$_3$), 3.69 (m, 4H; NCH), 4.22 (q, $J_{\mathrm{H,H}} = 7.2$ Hz, 2H; CH$_2$), 4.27 (q, $J_{\mathrm{H,H}} = 7.2$ Hz, 4H; CH$_2$), 5.86 (s, 10H; CH$_{\mathrm{Cp}}$), 7.02–7.56 (m, 3H; CH$_{\mathrm{arom}}$), 8.49 (m, 1H; CH$_{\mathrm{arom}}$), 10.64 (d, $J_{\mathrm{H,P}} = 4.8$ Hz, 1H; NH); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 14.7$, 14.9 (s; OCH$_2$*C*H$_3$), 24.5 (d, $J_{\mathrm{C,P}} = 6.3$ Hz; CH$_3$), 24.8 (d, $J_{\mathrm{C,P}} = 6.6$ Hz; CH$_3$), 49.3 (d, $J_{\mathrm{C,P}} = 12.3$ Hz; NCH), 60.7, 61.4 (s; CH$_2$), 111.4 (s; CH$_{\mathrm{Cp}}$), 118.7 (s; =C), 123.5, 129.6, 141.6 (s; CH$_{\mathrm{arom}}$), 130.4 (d, $J_{\mathrm{C,P}} = 24.4$ Hz; CH$_{\mathrm{arom}}$), 146.1 (s; Zr*C*CO$_2$Et), 147.3 (d, $J_{\mathrm{C,P}} = 30.1$ Hz; ZrC*C*), 164.7, 164.8 (s; C=O), 197.8 (d, $J_{\mathrm{C,P}} = 6.7$ Hz; ZrC), 202.0 (d, $J_{\mathrm{C,P}} = 40.2$ Hz; PC=N); elemental analysis calcd for $\mathrm{C_{41}H_{58}O_6N_3PZr}$ (811.10) (%): C 60.71, H 7.20, N 5.18; found: C 60.76, H 7.18, N 5.21.

18: Yellow solid, 0.456 g (78 % yield). IR (KBr): $\tilde{\nu} = 1561$ ν(C=N), 1710 ν(C=O), 3305 cm^{-1} ν(N–H); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 38.3$ (s); ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 0.97$ (d, $J_{\mathrm{H,H}} = 6.8$ Hz, 6H; CH$_3$), 1.02 (d, $J_{\mathrm{H,H}} = 6.5$ Hz, 6H; CH$_3$), 1.10 (m, CH$_3$, 9H; OCH$_2$C*H*$_3$), 1.37 (d, $J_{\mathrm{H,H}} = 6.5$ Hz, 6H; CH$_3$), 3.57 (s, 3H; OCH$_3$), 3.82 (m, 4H; NCH), 4.15 (q, $J_{\mathrm{H,H}} = 7.1$ Hz, 2H; CH$_2$), 5.88 (s, 10H; CH$_{\mathrm{Cp}}$), 6.99–7.53 (m, 3H; CH$_{\mathrm{arom}}$), 7.79 (s; =CH), 8.53 (m, 1H; CH$_{\mathrm{arom}}$), 11.22 (d, $J_{\mathrm{H,P}} = 5.0$ Hz, 1H; NH); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 14.9$ (s; OCH$_2$*C*H$_3$), 24.7 (d, $J_{\mathrm{C,P}} = 6.4$ Hz; CH$_3$), 24.9 (d, $J_{\mathrm{C,P}} = 6.6$ Hz; CH$_3$), 49.2 (d, $J_{\mathrm{C,P}} = 12.7$ Hz; NCH), 51.3 (s; OCH$_3$), 60.3 (s; CH$_2$), 111.6 (s; CH$_{\mathrm{Cp}}$), 117.3 (s; =CH), 123.2, 129.9, 140.9 (s; CH$_{\mathrm{arom}}$), 130.4 (d $J_{\mathrm{C,P}} = 26.7$ Hz; CH$_{\mathrm{arom}}$), 144.7, 145.3 (s; Zr*C*CO$_2$Et, =C), 147.5 (d, $J_{\mathrm{C,P}} = 32.7$ Hz; ZrC*C*), 163.5, 163.9 (s; C=O), 198.9 (d, $J_{\mathrm{C,P}} = 7.9$ Hz; ZrC), 201.5 (d, $J_{\mathrm{C,P}} = 41.2$ Hz; PC=N); elemental analysis calcd for $\mathrm{C_{37}H_{52}O_4N_3PZr}$ (725.01) (%): C 61.29, H 7.22, N 5.79; found: C 61.25, H 7.16, N 5.83.

21, **23**: Chlorophosphane **20** (0.056 mL, 0.311 mmol) was added at room temperature to a solution of **5a** (0.208 g, 0.311 mmol) in toluene (5 mL). The mixture was stirred at room temperature for 1 h and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatile components were removed from the solution to give **21** and **23** as the unique products of the reaction according to ^{31}P NMR spectroscopy. Compound **23** was identified in the reaction mixture by comparison with an authentical sample.[22] Independently, addition of HCl to **4a** allowed the preparation and isolation of **21** as a yellow solid: IR (KBr): $\tilde{\nu} = 1576$ ν(C=N), 3305 cm^{-1} ν(N–H); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 58.2$ (s); ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 1.11$ (d, $J_{\mathrm{H,H}} = 6.6$ Hz, 12H; CH$_3$), 1.21 (d, $J_{\mathrm{H,H}} = 6.6$ Hz, 12H; CH$_3$), 3.27 (d sept, $J_{\mathrm{H,H}} = 6.6$ Hz, $J_{\mathrm{H,P}} = 12.1$ Hz, 4H; NCH), 5.90 (s, 10H; CH$_{\mathrm{Cp}}$), 7.20 (m, 2H; CH$_{\mathrm{arom}}$), 7.88 (m, 4H; CH$_{\mathrm{arom}}$), 8.25 (m, 1H; CH$_{\mathrm{arom}}$), 10.12 (d, $J_{\mathrm{H,P}} = 5.0$ Hz, 1H; NH); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 24.4$ (d, $J_{\mathrm{C,P}} = 6.8$ Hz; CH$_3$), 25.1 (d, $J_{\mathrm{C,P}} = 5.0$ Hz; CH$_3$), 49.6 (d, $J_{\mathrm{C,P}} = 11.2$ Hz; NCH), 111.3 (s; CH$_{\mathrm{Cp}}$), 122.8, 129.8, 141.2 (s; CH$_{\mathrm{arom}}$), 130.1 (d, $J_{\mathrm{C,P}} = 14.3$ Hz; CH$_{\mathrm{arom}}$), 146.1 (d, $J_{\mathrm{C,P}} = 24.1$ Hz; ZrC*C*), 198.6 (d, $J_{\mathrm{C,P}} = 6.3$ Hz; ZrC), 202.5 (d, $J_{\mathrm{C,P}} = 40.6$ Hz; PC=N).

X-ray crystal structure analysis of **14** ($\mathrm{C_{44}H_{49}N_6O_3PZr \cdot 1.5\,C_6H_6}$): $M_r = 979.72$, monoclinic, space group $P2_1/n$, $T = 160$ K, $a = 13.811(6)$, $b = 18.356(5)$, $c = 20.031(8)$ Å, $\beta = 98.26(5)°$, $V = 5025(3)$ Å^3, $Z = 4$, $\mu = 0.296$ mm^{-1}. Of 27371 reflections collected, 6500 were independent; $R_{\mathrm{int}} = 0.0970$; final R indices: $R1 = 0.0402$, $wR2 = 0.0889$ ($I > 2\sigma(I)$), $R1 = 0.0729$, $wR2 = 0.0992$ (all data). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149738. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Hybrid Coordination Polymers—Metal Oxide Compounds with Chiral Structures[**]

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Many investigations of the design and synthesis of metal–organic compounds with porous structures have been motivated by potential applications in molecule recognition, separation, and catalysis.[1–11] By using rigid, multifunctional ligands, two- or three-dimensional microporous coordination polymers have been obtained with desired pore sizes and shapes.[3–11] Other metal–organic frameworks have been reported that, though they may have other valuable properties, are not microporous because of lattice interpenetration,[12] or are unstable on removal or exchange of their guest molecules or ions. Very few examples of either framework or microporous chiral metal–organic structures have been reported.[13–17]

One strategy to enhance the stability with respect to removal of the guest species is to attach the metal–organic components to a thermally more stable inorganic backbone. Several examples of compounds of this type containing both ligated metal cation and metal oxide components are known.[18–20] These extended lattices are formed in different ways, for example, by connecting a metal oxide cluster with a coordination complex, a metal oxide cluster anion with a coordination polymer, a metal oxide lattice with an isolated coordination complex, and metal oxide lattice with a coordination polymer. All of the inorganic components in the known examples are molybdenum or vanadium oxides.[18–20]

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