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Bridging N-Aminoisocyanate Ligands in Heterobimetallic Complexes: Coupling of Zirconium Hydrazinediides and Transition-Metal Carbonyls

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Summary: Reaction of the zirconium complex $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(=\text{NNPh}_2)(\text{py})]$ with metal carbonyl complexes yielded the heteronuclear complexes $[(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\text{py})\text{Zr}\{\mu\text{-OCNNPh}_2\text{-}1\kappa\text{C:}2\kappa^2\text{NO}\}\text{M}_m(\text{CO})_n]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ($m = 1, n = 5$), Fe ($m = 1, n = 4$), Mn ($m = 2, n = 9$)). The bridging *N*-aminoisocyanato ligands in the dinuclear complexes were formed by $[2 + 2]$ cycloaddition of the $\text{Zr}=\text{NNR}_2$ unit and coordinated CO.

Transition-metal hydrazides are key intermediates in the reductive activation of dinitrogen and as such have been extensively studied, especially for the group 6 metals.¹ A systematic investigation into the chemistry of group 4 metal hydrazides, in particular hydrazinediides, is a more recent development² which has been fueled by the activity of titanium complexes as catalysts for the hydrohydrazination of carbon–carbon multiple bonds³ and related multicomponent reactions.⁴

Two interrelated general patterns of reactivity of hydrazinediido ligands bonded to group 4 metals have emerged to date. Whereas alkynes, allenes, and heteroallenes undergo formal $[2 + 2]$ cycloadditions to the $\text{M}=\text{N}-\text{NR}_2$ units (and

possible concomitant or subsequent N–N bond cleavage),⁵ unsaturated polar substrates or molecular fragments such as isonitriles and chalcogen atom donors readily induce N–N bond cleavage.⁶ The reaction of a zirconium hydrazinediido with CO to give an isocyanato complex upon N–N bond cleavage was first described by Bergman et al.,⁷ and we also observed similar behavior for an amidozirconium complex containing the related *N*-pyridinioimido ligand.⁸ In this work we aimed to investigate the reaction of metal-bonded CO ligands in binary metal carbonyls with the previously reported zirconium hydrazinediido complex $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(=\text{NNPh}_2)(\text{py})]$ (**1**).⁹ It was of particular interest to assess whether the carbonyl complex would act merely as a CO donor, eventually giving the isocyanate, or remained intact, leading to isolable heterobimetallic coupling products.

Reaction of the zirconium complex **1** with 1 molar equiv of the corresponding mononuclear metal carbonyl complex yielded the heterodinuclear complexes **2a–c** and **3** (Scheme 1). The analytical data as well as the ¹H and ¹³C NMR and IR spectroscopic data of the four compounds are consistent with the generation of complexes containing bridging *N*-aminoisocyanato $\{\mu\text{-OCNNPh}_2\text{-}1\kappa\text{C:}2\kappa^2\text{NO}\}$ ligands¹⁰ formed by $[2 + 2]$ cycloaddition of the $\text{Zr}=\text{NNR}_2$ unit and coordinated CO, as indicated for the molecular structures depicted in Scheme 1. The bridging *N*-aminoisocyanato units are characterized by remarkable ¹³C NMR downfield shifts (**2a** δ 284.0, **2b** δ 277.5, **2c** δ 266.5, **3** δ 271.7) of their central carbon atoms, which may indicate a partial carbene character of these CO-derived carbon atoms (vide infra). In order to establish the structural details of this new class of compounds and to obtain additional structural information to elucidate the bonding in the bridging $\{\text{OCNNPh}_2\}$ ligand, single-crystal X-ray structure analyses

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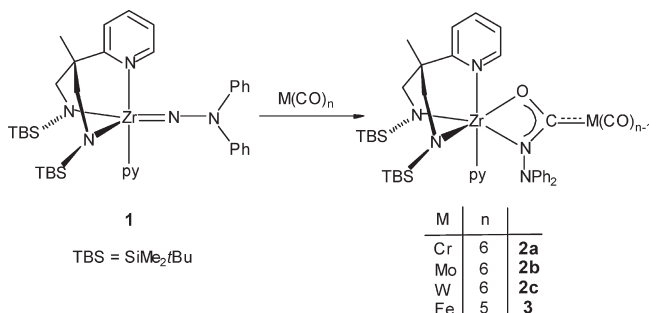
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Scheme 1. Synthesis of Complexes **2a–c** and **3**

of complexes **2a** and **3** were carried out.¹¹ The molecular structures of **2a** and **3** are depicted in Figure 1, and a comparative listing of the principal bond lengths and angles is provided in Table 1.

The structural arrangement of the Zr unit in both **2a** and **3** (Figure 1) may not be readily identified with the usual deltahedral coordination geometries for 6-fold coordination. The ancillary diamidopyridyl ligand coordinates facially to the zirconium atom in both systems, thus protecting a significant sector in the coordination sphere of the early transition metal. Its pyridine N atom N(3), the donor atoms O(1) and N(4) of the bridging κ^2 N,O-coordinated {OCNNPh₂} ligand, and the pyridine N(6) are located in an intramolecular plane which coincides with an overall approximate molecular mirror plane for complex **2a**. The amido N atoms N(1) and N(2) as well as Zr(1) span a second plane which is close to orthogonal to the former. An arrangement of donor atoms, as found for the zirconium moiety in **2a** and **3**, is obtained upon removal of two vertices in a (distorted) triangulated dodecahedron (coordination number 8) and represents a rare structural feature in coordination chemistry. The C(1)–Cr(1) distance (2.068(2) [2.074(2)] Å) in **2a** and the C(1)–Fe(1) bond length (1.995(1) Å) in **3** are slightly greater than the average distances in previously characterized chromium and iron Fischer carbene complexes in general.¹² However, these slightly increased bond lengths are typical for mixed alkoxy-/aminocarbene complexes for which the metal–carbon bond order is significantly decreased due to the two π -donor substituents.¹³

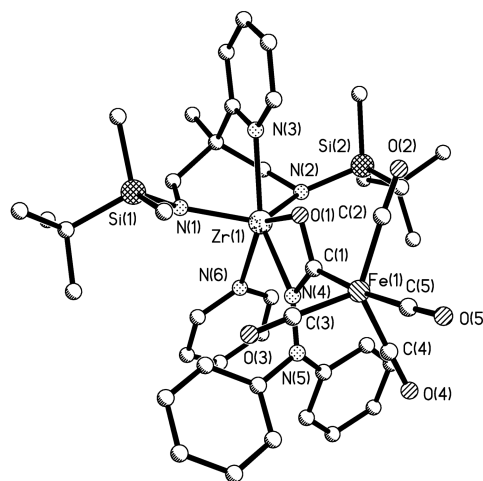
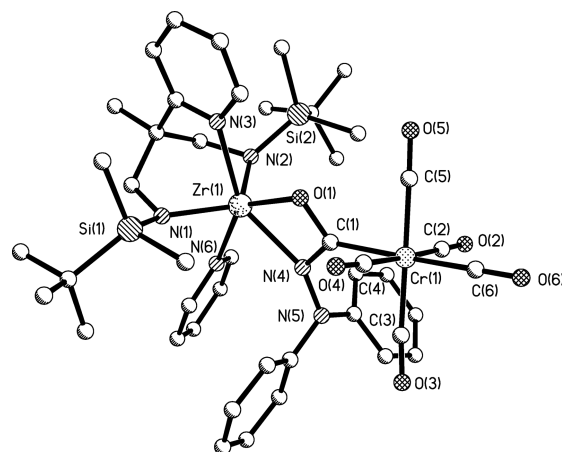


Figure 1. Molecular structures of complexes **2a** (top) and **3** (bottom). H atoms have been omitted for clarity. Only one of the two independent molecules of **2a** in the crystal is displayed. A comparative listing of selected bond lengths and angles is provided in Table 1.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Complexes **2a**, **3**, and **4**

bond length or angle	2a ^a	3	4
Zr(1)–N(4)	2.242(2) [2.259(2)]	2.247(1)	2.276(2)
Zr(1)–O(1)	2.088(2) [2.083(2)]	2.086(1)	2.083(1)
N(4)–N(5)	1.411(3) [1.418(3)]	1.409(1)	1.415(2)
C(1)–O(1)	1.348(3) [1.349(3)]	1.338(1)	1.344(2)
C(1)–N(4)	1.340(3) [1.331(3)]	1.345(1)	1.341(2)
TM(1)–C(1) ^b	2.068(2) [2.074(2)]	1.955(1)	1.964(2)
TM(1)–TM(2)			2.899(1)
Zr(1)–O(1)–C(1)	101.0(1) [101.1(1)]	101.4(7)	101.9(1)
Zr(1)–N(4)–C(1)	94.1(1) [93.5(1)]	93.6(7)	93.0(1)
TM(1)–C(1)–O(1)	120.1(2) [119.2(2)]	120.6(8)	118.3(1)
TM(1)–C(1)–N(4)	134.3(2) [134.9(2)]	133.6(8)	135.6(1)
N(4)–C(1)–O(1)	105.6(2) [105.9(2)]	105.9(9)	106.1(1)

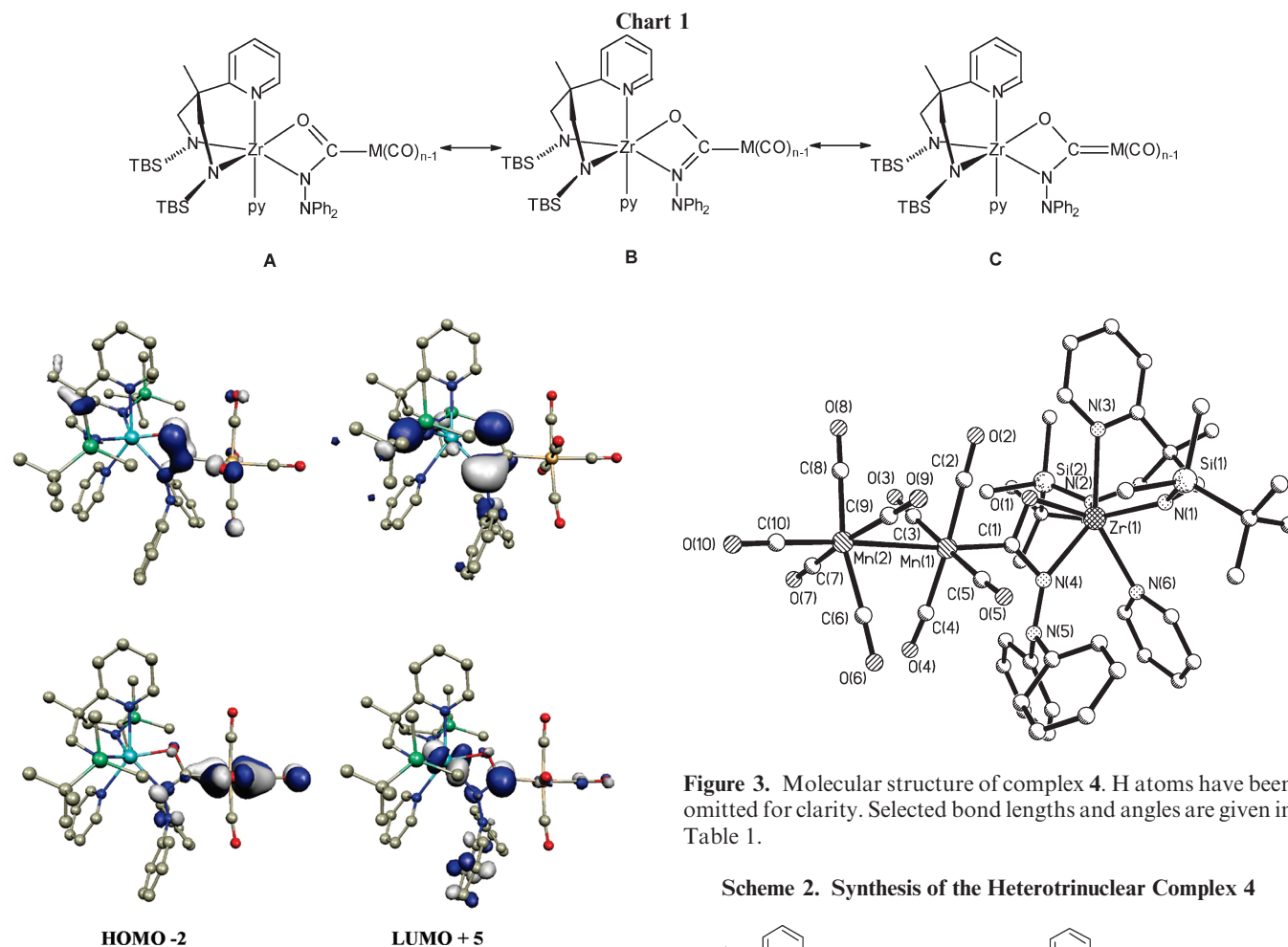
^a**2a** crystallizes with two independent molecules in the asymmetric unit. Values in brackets refer to the second molecule. ^bTM = transition metal.

In both complexes **2a** and **3** the C(1)–O(1) distances (**2a**, 1.348(3) [1.349(3)] Å; **3**, 1.338(1) Å) as well as the C(1)–N(4) bond lengths (**2a**, 1.340(3) [1.331(3)] Å; **3**, 1.345(1) Å) of the bridging ligand are consistent with some double-bond character, indicating bond delocalization within the {OCNNPh₂} ligand systems. As expected, C(1) is planar ($\sum \angle_{C(1)} = 360^\circ$),

(11) Crystallographic data are as follows. General information: all data sets collected with Mo K α radiation (graphite monochromator, $\lambda = 0.71073$ Å) at $T = 100(2)$ K. **2a**·1.5(toluene): C_{54.50}H₆₈CrN₆O₆Si₂Zr, monoclinic, space group Pn , $a = 11.239(5)$ Å, $b = 22.213(12)$ Å, $c = 22.686(11)$ Å, $\beta = 92.84(1)^\circ$, $V = 5657(5)$ Å³, $Z = 4$, $\mu = 0.470$ mm^{−1}, $F_{000} = 2308$; θ range 0.9–32.3°; reflections, 143 033 measured, 36 479 independent ($R_{int} = 0.0461$), 30 388 observed ($I > 2\sigma(I)$); final R indices ($F_o > 4\sigma(F_o)$) $R(F) = 0.0387$, $R_w(F^2) = 0.0970$; inversion twin, ratio 0.54(1). **3**: C₄₃H₅₆FeN₆O₅Si₂Zr, monoclinic, space group $P2_1/n$, $a = 12.784(5)$ Å, $b = 17.926(8)$ Å, $c = 20.567(9)$ Å, $\beta = 101.35(1)^\circ$, $V = 4621(3)$ Å³, $Z = 4$, $\mu = 0.640$ mm^{−1}, $F_{000} = 1960$; θ range 2.0–32.3°; reflections, 116 710 measured, 15 645 independent ($R_{int} = 0.0295$), 13 715 observed ($I > 2\sigma(I)$); final R indices ($F_o > 4\sigma(F_o)$) $R(F) = 0.0264$, $R_w(F^2) = 0.0779$. **4**·3(benzene): C₆₆H₇₄Mn₂N₆O₁₀Si₂Zr, monoclinic, space group $P2_1/n$, $a = 13.124(6)$ Å, $b = 24.356(12)$ Å, $c = 21.617(10)$ Å, $\beta = 104.47(1)^\circ$, $V = 6691(5)$ Å³, $Z = 4$, $\mu = 1.359$ mm^{−1}, $F_{000} = 2840$; θ range 1.3–32.3°; 169 507 reflections measured, 22 733 independent ($R_{int} = 0.0436$), 18 441 observed ($I > 2\sigma(I)$); final R indices ($F_o > 4\sigma(F_o)$) $R(F) = 0.0380$, $R_w(F^2) = 0.1055$.

(12) References of structures in CSD, Cambridge, Version 5.30, Update 3 (May 2008): containing Cr=C(OR) bonds, 284 examples, from 1.879 to 2.194 Å; containing Fe=C bonds, 140 examples, from 1.797 to 2.024 Å; containing Mn=C bonds, 85 examples, from 1.820 to 2.121 Å.

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whereas the central cyclic ZrNCO unit is slightly puckered in both complexes (**2a** -7.1° [-4.8°], **3** -1.3°), which we attribute to steric interaction between the two linked complex fragments. On the basis of these structural data the bonding situation was thought to be representable by the three resonance structures depicted in Chart 1.

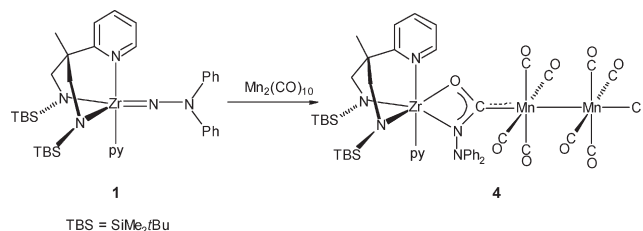
In order to obtain a more detailed picture of the bonding in the central bridging ligand generated by coupling of the hydrazide with a metal-bonded carbonyl ligand, a DFT study using the B3PW91 hybrid functional was carried out.¹⁴ The analysis of the Kohn–Sham molecular orbitals located on the central structural unit reveals significant C(1)–O(1) and C(1)–N(4) π -bonding (Figure 2, top), as noted for N–O heterocyclic carbenes, whereas the HOMO-2 clearly indicates the weak Cr–metal back-donation to C(1) and the π -system of the ZrNCO metallacycle (Figure 2, bottom).

This interpretation of the C(1)–C(1) carbene bonding is also confirmed by the Wiberg indices for all bonds in the central bridging ligand (Supporting Information).

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Figure 3. Molecular structure of complex **4**. H atoms have been omitted for clarity. Selected bond lengths and angles are given in Table 1.

Scheme 2. Synthesis of the Heterotrinnuclear Complex **4**



Furthermore, natural population analysis (NPA) has established the expected positive partial charge on C(1) ($q_{\text{NPA}} = +0.5$). Taking these results of the DFT study into account, we conclude that the resonance structures **A** and **B** in Chart 1 are to be attributed the greatest weight in the description of the {OCNNPh₂} ligand. Finally, the ¹³C NMR chemical shift of the C(1) resonance in **2a** (284 ppm) has been adequately modeled using the GIAO-B3PW91 computational tool¹⁵ (calibrated with reference to the average shifts of the equatorial carbonyl ligands), which gave a value of 286 ppm.

Similar reactivity of the hydrazinediido complex **1** toward metal carbonyl complexes, as described above for the mononuclear compounds, was observed with the dinuclear metal carbonyl [Mn₂(CO)₁₀] giving the corresponding trinnuclear complex **4** (Scheme 2). Exposure of [Mn₂(CO)₁₀] to an excess of hydrazide did not lead to further interligand coupling, which indicates a deactivation of the remaining carbonyl

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units caused by this transformation. As expected, the features of the molecular structure of **4**, which was determined by X-ray diffraction (Figure 3), do not differ significantly from those of its analogues derived from mononuclear carbonyl complexes.¹¹

The principal metric parameters are very similar (Mn(1)–C(1) = 1.964(2), C(1)–O(1) = 1.344(2), C(1)–N(4) = 1.341(2) Å; $\Sigma \angle_{C(1)} = 360.0^\circ$), and the ¹³C NMR signal of the central carbon nucleus in the bridging isocyanato fragment was also observed at very low field (279.3 ppm). In the only detectable isomer, the {OCNNPh₂} ligand coordinates in a trans disposition relative to the metal–metal bond, which can be explained by the sterics of both complex fragments.

Complexes **2a–c** and **3** (and, to a lesser degree, complex **4**) were found to be thermally stable up to 80 °C, where

nonspecific degradation set in. In no case did we observe the formation of the isocyanato complex analogous to species reported by Bergman⁷ or the complex we had previously obtained by reaction of a pyridinioimido complex with CO gas.⁸

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Supporting Information Available: Text, tables, and CIF files giving experimental procedures, characterization data for all new compounds, and crystallographic details for **2a**, **3**, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.