Organometallics **2003,** *22,* 387−389

Redefining the Coordination Geometry and Reactivity of Guanidinate Complexes by Covalently Linking the Guanidinate Ligands. Synthesis and Reactivity of $[RN\{NH(R)\}CN(CH_2)_2NC\{NH(R)\}NR]M(CH_2Ph)_2$ ($R = {}^iPr$; $M = Ti, Zr$)

Tiow-Gan Ong, Glenn P. A. Yap, and Darrin S. Richeson*

Department of Chemistry and the Center for Catalysis Research and Innovation,
University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

Received October 3, 2002

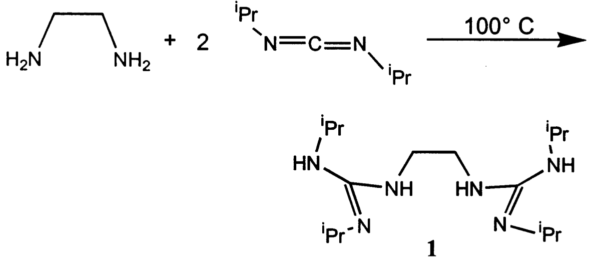
Summary: Reaction of the new biguanidine $({}^iPr)HN\{NH({}^iPr)\}CN(CH_2)_2NC\{NH({}^iPr)\}N({}^iPr)H$ (**1**) *with* $M(CH_2Ph)_4$ *affords the hydrocarbyl complexes* $[{}^iPrN\{NH({}^iPr)\}CN(CH_2)_2NC\{NH({}^iPr)\}N{}^iPr]M(CH_2Ph)_2$ ($[L_4{}^{Pr}]M(CH_2Ph)_4$; $M = Ti$ (**2**), Zr (**3**)). *Structure determinations of **2** and **3** and the reactivity of **3** with 2,6-dimethylphenyl isocyanide indicate that the linked guanidinate ligand system provides a more open metal coordination sphere than do the unlinked analogues.*

Controlling metal coordination environment and reactivity through modification of supporting ligation is a common theme in organometallic chemistry. Considerable recent interest has focused on the development of amidinate and guanidinate anions, $[N(R)C(R')N(R)]^-$ and $[N(R)C(NR'_2)N(R)]^-$, as sterically and electronically flexible ligands for the design of new transition-metal and main-group-metal complexes.[1,2] We have been particularly interested in these species for this role due to their amenability to modification through directed variation of the substituents, R and R′.[3] Despite this potential, the reaction chemistry of complexes possessing these ligands is still relatively undeveloped.

Synthetic and reactivity studies of transition-metal guanidinate complexes have focused on the mono(guanidinate) and bis(guanidinate) frameworks.[2] We are interested in further revealing the versatility of the guanidinate system by covalently linking two of these ligands as a means of further defining and constraining complex geometry. Such concepts have been elegantly applied to *ansa*-metallocene complexes[4] and other anionic functionalities including amidinates[5] and amidates.[6]

This contribution describes the first linked guanidinate ligand system and its application in group 4 organometallic chemistry. We demonstrate that tethering of the two guanidinate moieties results in changes to ligand geometry and metal coordination behavior and that the reactivity of these constrained complexes differ from that of their unlinked analogues.

The direct reaction of 2 equiv of diisopropylcarbodiimide with ethylenediamine in toluene at 100 °C produces, in 60% yield, biguanidine **1**, in which the two guanidine moieties are linked via an ethylene bridge (eq 1).



1

(1)

The direct synthesis of **1** from commercial reagents and the ready availability of other diamines with a variety of tethers should allow considerable flexibility for modifications to this potential ligand. Compound **1** possesses reactive NH groups that can be employed for its introduction to an appropriate metal complex. For example, **1** reacts smoothly with tetrakis(benzyl) complexes of Zr and Ti to yield complexes **2** and **3**, respectively (Scheme 1). The NMR spectra of **2** and **3** indicate that they possess a dianionic linked biguanidinate ligand and two benzyl groups. Furthermore, these spectral data indicate a symmetric bonding arrangement for the biguanidinate ligand, as exemplified by only two signals for the ^{i}Pr moieties and a single resonance for the ethylene bridge.

---

(1) For reviews of benzamidinate complexes see: (a) Edelmann, F. *Coord. Chem. Rev.* **1994**, *94*, 403. (b) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *94*, 219.

(2) For a recent review of guanidinate complexes see: Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*, 91.

(3) (a) Lu, Z.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2001**, *20*, 706. (b) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *J. Chem. Soc., Chem. Commun.* **2000**, 1515. (c) Thirupathi, N.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2000**, *19*, 2573. (d) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *J. Chem. Soc., Dalton Trans.* **2000**, 1663. (e) Foley, S. R.; Zhou, Y.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **2000**, *39*, 924. (f) Thirupathi, N.; Yap, G. P. A.; Richeson, D. S. *J. Chem. Soc., Chem. Commun.* **1999**, 2483.

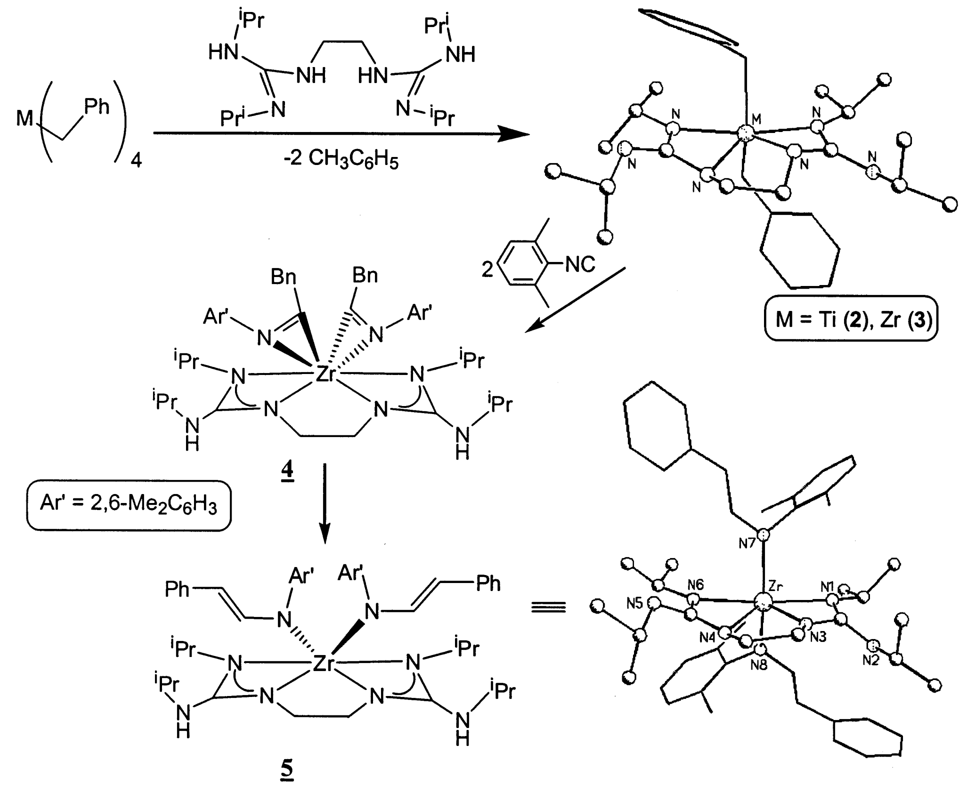
(4) For a recent examination of the effect of bridging groups in *ansa*-metallocenes see: Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525 and references therein.

(5) (a) Hagadorn, J. R. *Chem. Commun.* **2001**, 2144. (b) Chen, C.-T.; Rees, L. H.; Cowley, A. R.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **2001**, 1761. (c) Bambirra, S.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2001**, *20*, 782. (d) Bambirra, S.; Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 3197. (e) Hagadorn, J. R.; Arnold, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1729. (f) Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Eur. J. Inorg. Chem.* **1998**, 1867.

(6) Giesbrecht, G. R.; Shafir, A.; Arnold, J. *Inorg. Chem.* **2001**, *40*, 6069.

10.1021/om020830g CCC: \$25.00

Scheme 1



Compounds **2** and **3** are related to the reported unlinked bis(guanidinate) complexes $\{(Me_2N)C(N^iPr)_2\}_2M(CH_2Ph)_2$ (M = Ti (**I**), Zr (**II**)) and $[\{(^iPrNH)C(N^iPr)_2\}_2Zr(CH_2Ph)_2]$ (**III**).[7,8] These recently reported species exhibit structures with two chelating bidentate guanidinate ligands and cis-oriented hydrocarbyl groups, resulting in pseudo-C_2-symmetric, distorted-octahedral-based coordination geometries.

The single-crystal X-ray structures of **2** and **3** revealed that these two species exhibit similar molecular structures and that they differ substantially from **I**–**III**. Consistent with their spectroscopic data, both of these new complexes possess two benzyl groups and a chelating tetradentate dianionic version of biguanidine **1**.[9,10] The biguanidinate ligand in both **2** and **3** coordinates to the metal center in a symmetrical fashion to yield an MN_4 arrangement that approaches planarity. This coordination geometry is in striking contrast to the structurally characterized unlinked bis(guanidinate) species **I**–**III**. Specifically, the angles between the two planar four-membered guanidinate chelate rings in **2** and **3** are approximately 20°, while for a typical unlinked example such as **II** this angle is 99.3°. This considerable change in coordination behavior is attributed to the restrictions of the ethylene linkage of the biguanidinate ligand.

Linking the guanidinate moieties has the effect of opening the metal coordination sphere, as indicated by an increase in the angle between the two benzyl ligands in comparison with the unlinked analogues. For example, the angles between the two undistorted η^1-benzyl groups in complexes **2** and **3** (i.e. CH_2MCH_2) are 134.2(1) and 128.4(2)°, respectively, while the corresponding angles in **I** (88.6(2)°), **II** (89.7(1)°), and **III** (93.02(7)°) are much smaller and are in accordance with the distorted-octahedral geometries of these species.

We anticipated that the observed changes in coordination geometry that accompany the tethering of the two guanidinate ligands should have important reactivity consequences. To probe this concept, we chose to investigate the fundamental reactivity of these new biguanidinate species with 2,6-dimethylphenyl isocyanide (Ar′NC). Aryl isocyanides react with unlinked bis(guanidinate) species, including **I**–**III**, by initially undergoing insertion reactions with the hydrocarbyl moieties forming η^2-iminoacyl ligands for which subsequent transformations have been observed.[8] This reactivity serves as a benchmark for comparison with the reactivity of **3** and Ar′NC that is summarized in Scheme 1.[11]

Complex **3** reacts at room temperature with 2 equiv of Ar′NC within 1 h to yield the new bis(η^2-iminoacyl) complex **4** (Scheme 1). A ^{13}C NMR resonance for **4** at δ 257.7 is assigned to the two equivalent iminoacyl ligands, and the relative integration intensities observed in the ^1H NMR spectra of this compound suggest the proposed empirical formula. A single-crystal X-ray

---

(7) (a) Mullins, S. M.; Duncan, A. P.; Bergman, R. G.; Arnold, J. *Inorg. Chem.* **2001**, *40*, 6952. (b) Duncan, A. P.; Mullins, S. M.; Arnold, J.; Bergman, R. G. *Organometallics* **2001**, *20*, 1808.

(8) (a) Ong, T.-G.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 1. (b) Ong, T.-G.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 2839–2841.

(9) Crystals were obtained from a saturated toluene solution cooled to −35 °C. Crystal data for **2**: empirical formula $C_{30}H_{48}N_6Ti$, $T = 203(2)$ K, $\lambda = 0.710\ 73$ Å, space group $P2_12_12_1$, $a = 12.440(4)$ Å, $b = 14.820(3)$ Å, $c = 16.836(5)$ Å, $V = 3103.9(15)$ Å^3, $Z = 4$, R indices ($I > 2\sigma(I)$) R1 = 0.0414 and wR2 = 0.0992. The structure was refined as a racemic twin with a refined absolute structure parameter of 0.62(3).

(10) Crystals were obtained from a saturated toluene solution cooled to −35 °C. Crystal data for **3**: empirical formula $C_{30}H_{48}N_6Zr$, $T = 203(2)$ K, $\lambda = 0.710\ 73$ Å, space group $P2_12_12_1$, $a = 12.6201(19)$ Å, $b = 14.985(2)$ Å, $c = 16.743(3)$ Å, $V = 3166.2(8)$ Å^3, $Z = 4$, R indices ($I > 2\sigma(I)$) R1 = 0.0442 and wR2 = 0. 0882.

structural analysis has confirmed the proposed structure.[12] This reactivity is consistent with that observed for the bis(guanidinate) dimethyl complex [{(Me_2N)C(N^iPr)$_2$}$_2$ZrMe_2], which produced the bis(iminoacyl) species [{(Me_2N)C(N^iPr)$_2$}$_2$Zr(η^2-Ar′N=CMe)$_2$] (**IV**) when reacted with 2 equiv of Ar′NC.[8(a)]

The subsequent reactivity of **4** diverges from that observed for **IV**, and we attribute this to the linking of the guanidinate ligands. Mild thermolysis of **IV** transforms the two η^2-iminoacyl groups into a metal-bound enediamido ligand via a coupling reaction.[8a,13] In contrast, the product isolated when complex **4** is heated to 90 °C displays ^{1}H and ^{13}C NMR spectra, indicating that both iminoacyl groups have transformed, via an overall 1,2-hydrogen shift, into vinylamido groups. A resonance for the vinylic proton adjacent to the phenyl group appears at δ 4.81, while the other vinylic proton that is adjacent to the amido nitrogen exhibits a more downfield shift at δ 7.87. The coupling between these two protons of 14 Hz is consistent with a trans arrangement for the olefin. The ^{13}C NMR resonance for the iminoacyl has disappeared and is replaced with two signals for the vinylic carbon atoms at δ 98.1 (NAr′CH=*C*HPh) and 150.1 (NAr′*C*H=CHPh).

The structure of **5** was determined and confirmed the presence of the trans vinylamido groups and the biguanidinate dianion (Scheme 1).[14] The Zr coordination geometry in **5** is nearly identical with that observed for **3**; the biguanidinate ligand exhibited nearly identical metrical parameters for the two compounds, and the vinylamido groups of **5** occupy coordination sites similar to those of the benzyl ligands in **3** (N(7)−Zr−N(8) angle of 137.63(13)°). Conjugation of the nitrogen lone pair with the vinyl moieties is suggested by the short N−C(vinyl) bond lengths (1.388(5) and 1.392(5) Å), the planar N(7) and N(8), and the slightly elongated Zr−N distances of 2.176(3) Å.

The only reported precedent for this type of iminoacyl rearrangement involves complexes derived for the reaction of Ar′NC with $Cp_2M(CH_2\text{-py-Me})_2$ (M = Zr, Hf; CH_2-py-Me = 2-(6-methylpyridyl)methyl). After initially generating iminoacyl complexes, these species ultimately yield the vinylamido complexes Cp_2M(Ar′NCH=CH-py-Me)(CH_2-py-Me) and Cp_2M(Ar′NCH=CH-py-Me)$_2$, depending on the reaction stoichiometry.[15] On the basis of mechanistic studies, it appears that the coordination of the pyridine nitrogen of the hydrocarbyl ligands plays an important role in facilitating this isomerization. Interestingly, low-temperature addition of pyridine to the η^2-acyl complex Cp*TaCl_3(η^2-COCH_2-CMe_3) initially yields a pyridine adduct that isomerizes to the enolate Cp*TaCl_3(py)(η^2-OCH=CHCMe_3) at −10 °C.[16]

We attribute the difference in reactivity between **4** and **IV** to the more open coordination environment of **4** that is provided by the biguanidinate ligand. This may facilitate the observed conversion by allowing coordination of an external base to complex **4**. One source of such external ligands is provided by the uncoordinated nitrogen centers of the biguanidinate ligand. We are still attempting to clarify the mechanistic details for the formation of **5** but can report that addition to pyridine to a solution NMR sample of **4** in C_6D_6 appears to only slightly accelerate its transformation to **5**.

We have demonstrated that linking guanidinate ligands via a covalent tether can alter the relative orientation of the ligand array, open the metal coordination sphere relative to the analogous unbridged systems, and have significant effects on the reactivity of metal complexes. Biguanidinate ligands can be prepared from commercial sources and should be amenable to straightforward modification of the linkage and nitrogen substituents. We expect that biguanidinates will form an interesting set of ancillary ligands for new transition-metal and lanthanide chemistry.

Acknowledgment. This work was supported by the NSERC of Canada.

Supporting Information Available: Text giving experimental details for compounds **1**−**5** and thermal ellipsoid plots and tables of crystal data and structural solution and refinement details, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds **2, 3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020830G

---

(11) For a review of the insertion chemistry of isocyanides see: Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059 and references therein.

(12) The single-crystal X-ray structure for compound **4** has been determined. Full structural details will be reported in a future paper.

(13) The intramolecular coupling between two η^2-iminoacyl groups to yield enediamido ligands has been observed for group 4 complexes with a variety of supporting ligand environments: Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068. Durfee, L. D.; McMullen, A. K.; Rothwell, I. P. *J. Am. Chem. Soc.* **1988**, *110*, 1463. Scott, M. J.; Lippard, S. J. *Organometallics* **1997**, *16*, 5857. Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 9709.

(14) Crystals were obtained from a saturated toluene solution cooled to −35 °C. Crystal data: empirical formula $C_{48}H_{64}N_8Zr$, $T = 203(2)$ K, $\lambda = 0.710\,73$ Å, space group $P2_1/n$, $a = 14.5031(14)$ Å, $b = 18.1977(18)$ Å, $c = 17.9802(18)$ Å, $\beta = 104.504(2)°$, $V = 4594.2(8)$ Å^3, $Z = 4$, R indices ($I > 2\sigma(I)$) R1 = 0.0608 and wR2 = 0.1399.

(15) Beshouri, S. M.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 2375. Beshouri, S. M.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1987**, *6*, 891.

(16) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 149.