ORGANOMETALLICS

Chemistry of oxophilic transition metals. 4. Reactivity of the organozirconium(III) complex (.mu.-.eta.5:.eta.5-C10H8)[(.mu.-Cl)Zr(.eta.5-C5H5)]2 with diphenyldiazomethane, tert-butyl isocyanide, and trimethylsilyl azide: diazo, cyano, and imido complexes

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Chemistry of Oxophilic Transition Metals. 4.[†] Reactivity of the Organozirconium(III) Complex $(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)[(\mu\text{-}Cl)Zr(\eta^5\text{-}C_5H_5)]_2$ with Diphenyldiazomethane, *tert*-Butyl Isocyanide, and Trimethylsilyl Azide: Diazo, Cyano, and Imido Complexes

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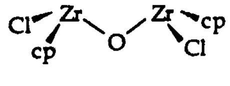
The fulvalene zirconium(III) complex $(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)[(\mu\text{-}Cl)Zr(\eta^5\text{-}C_5H_5)]_2$ (**1**) reacts with stoichiometric amounts of diphenyldiazomethane, $N_2{=}C(C_6H_5)_2$, and with *tert*-butyl isocyanide, $C{\equiv}NC(CH_3)_3$, to give the 1:1 addition products $[\mu\text{-}\eta^1\text{:}\eta^2\text{-}N_2(C_6H_5)_2](\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)ZrCl]_2$ (**3**) and $[\mu\text{-}\eta^1\text{:}\eta^2\text{-}CNC(CH_3)_3](\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)ZrCl]_2$ (**4**), respectively. On the other hand, the reaction of **1** with trimethylsilyl azide, $(CH_3)_3SiN_3$, takes place under loss of molecular nitrogen, yielding a mixture of $(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)ZrCl_2]_2$ (**5**) and $(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)[(\mu\text{-}NSi(CH_3)_3)Zr(\eta^5\text{-}C_5H_5)]_2$ (**6**). The crystal and molecular structures of **3** and **4** have been determined by X-ray diffraction methods. **3** crystallizes in a triclinic unit cell of $P\bar{1}$ symmetry with $a = 9.189$ (1) Å, $b = 10.808$ (1) Å, $c = 15.833$ (1) Å, $\alpha = 104.93$ (1)°, $\beta = 100.35$ (1)°, $\gamma = 97.82$ (1)°, $V = 1467$ Å^3, $Z = 2$, and $d_{calc} = 1.598$ g cm^{-3}. **4** crystallizes in an orthorhombic crystal lattice of $P2_12_12_1$ symmetry with $a = 8.233$ (1) Å, $b = 16.891$ (2) Å, $c = 17.312$ (2) Å, $V = 2407$ Å^3, $Z = 4$, and $d_{calc} = 1.641$ g cm^{-3}. Both structures can be regarded as a result of diphenyldiazomethane and *tert*-butyl isocyanide insertion into the Zr–Zr bond of **1** with concomitant splitting (opening) of the chloride bridges. The unsaturated organic molecule acts as a bridging ligand, coordinated in a $(\sigma + \pi)$ fashion. Sodium amalgam reduction of **4** in the presence of $C{\equiv}NC(CH_3)_3$ unexpectedly yields the cyano complex $(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)[(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CN)Zr(\eta^5\text{-}C_5H_5)]_2$ (**8**), whose structure has been inferred from IR and ^1H and ^{13}C NMR spectroscopic data.

Introduction

The organometallic chemistry of group 4 metals is virtually based on the bent Mcp_2 metallocene fragment[1] (cp denotes the π-bonded cyclopentadienyl (C_5H_5) ligand), which doubtless figures among the best known organometallic systems.[2] The ability of the Mcp_2 moiety to accomplish unusual coordination modes when attached to unsaturated molecules as well as to achieve profound structural changes and transformations of the latter has been correlated with the number and spatial disposition of its frontier orbitals.[3] Considering the current general interest in the potential cooperative effect exerted on simple molecules by two close, reactive metal centers,[4] it is certainly surprising that homodinuclear systems of related nature have only recently drawn enough attention to be the subject of a MO study.[5]

We have reported a facile, high-yield synthesis of $(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)[(\mu\text{-}Cl)Zr(\eta^5\text{-}C_5H_5)]_2$ (**1**),[6] a thermally stable, air- and moisture-sensitive compound in which two very reactive Zr(III) centers are held together by a fulvalene group. This ligand has been revealed as a convenient binucleating agent[7] and is thought to play a central role in the stabilization of **1**.[8,9]

As **1** readily reacts with molecular oxygen to give $(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu\text{-}O)[(\eta^5\text{-}C_5H_5)ZrCl]_2$ (**2**),[6a] we sought to synthesize related homodinuclear compounds containing an additional bridging unit of the isoelectronic series O/NR/CR_2. Reasonable sources of carbene (CR_2) and nitrene (NR) fragments are diazo compounds ($N_2{=}CR_2$)[10] and organic azides (RN_3),[11] respectively. Here, we report on



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[†] For part 3 of this series, see ref 12.

[‡] Alexander von Humboldt Junior Research Fellow, 1986–87.

(1) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood: Chichester, U.K., 1986. Bottill, M.; Gavens, P. D.; Kelland, J. W.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 3.

(2) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(3) Hofmann, P.; Stauffert, P.; Frede, M.; Tatsumi, K. *Chem. Ber.* **1989**, *122*, 1559. Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.

(4) For leading references: Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41. Casey, C. P.; Bullock, R. M. *Acc. Chem. Res.* **1987**, *20*, 167. Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 6, p 763.

(5) Pavan Kumar, P. N. V.; Jemmis, E. D. *J. Am. Chem. Soc.* **1988**, *110*, 125.

(6) Original reports: (a) Asworth, T. V.; Cuenca, T.; Herdtweck, E.; Herrmann, W. A. *Angew. Chem.* **1986**, *98*, 278; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 289. (b) Cuenca, T.; Herrmann, W. A.; Asworth, T. V. *Organometallics* **1986**, *5*, 2514. Succeeding report: (c) Gambarotta, S.; Chiang, M. Y. *Ibid.* **1987**, *6*, 897.

(7) Jutzi, P.; Schnittger, J. *Chem. Ber.* **1989**, *122*, 629. Herrmann, W. A.; Andrejewski, D.; Herdtweck, E. *J. Organomet. Chem.* **1987**, *319*, 183. Drage, J. S.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 280. Huffmann, M. A.; Newman, D. A.; Tilset, M.; Tolman, W. B.; Vollhardt, K. P. C. *Ibid.* **1986**, *5*, 1926. Egan, J. W.; Peterson, J. L. *Ibid.* **1986**, *5*, 906. Spink, W. C.; Rausch, M. D. *J. Organomet. Chem.* **1986**, *308*, C1. Escher, A.; Rutsch, W.; Neuenschwander, M. *Helv. Chim. Acta* **1986**, *69*, 1644. For earlier examples see ref 6b.

(8) Cf. the proclivity of the related $[cp_2Zr(\mu\text{-}Cl)]_2$ to undergo disproportionation in solution even at −20 °C. See ref 9.

(9) Wielstra, Y.; Gambarotta, S.; Meetsma, A.; Spek, A. L. *Organometallics* **1989**, *8*, 2948.

(10) Reviews: (a) Herrmann, W. A. *Angew. Chem.* **1978**, *90*, 855; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800. (b) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

(11) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985.

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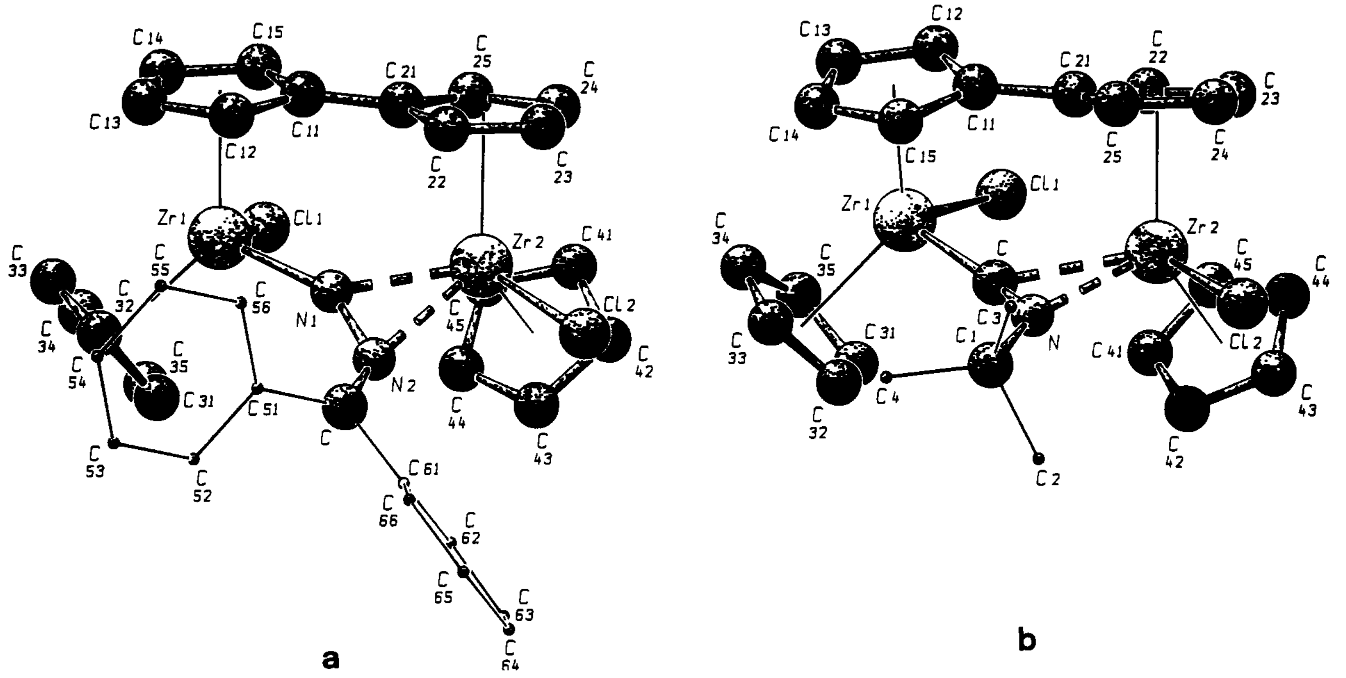

Figure 1. SCHAKAL drawings of complexes 3 (a; left side) and 4 (b; right side). Hydrogen atoms have been omitted for clarity.

the reactivity of 1 toward diphenyldiazomethane, *tert*-butyl isocyanide, a carbene-like molecule, and trimethylsilyl azide. Some of the present results have already been briefly communicated.[12]

Results and Discussion

(a) Reaction of 1 with Diphenyldiazomethane. Addition of $N_2{=}C(C_6H_5)_2$ to a toluene solution of 1 at 70 °C results in an immediate color change from deep violet to bright red. After workup of the solution, 3 is obtained as orange crystals in good yields (65%) according to Scheme I.

The fact that no gas evolution was observed during the reaction, together with the elemental analyses of 3, pointed out that in the present case diphenyldiazomethane forms a 1:1 adduct in its structurally intact form, rather than acting as a source of the carbene fragment $:CPh_2$. Considering the high versatility of diazoalkanes as ligands in transition-metal chemistry,[10] an X-ray diffraction analysis was carried out on 3 as the only unequivocal proof of structure.

Figure 1a shows a SCHAKAL view of the binuclear complex 3. Important structural and atomic positional parameters are listed in Tables I and II, respectively. The two Zr atoms are coordinated to the same side of the fulvalene ligand and bridged further by an $\eta^1{:}\eta^2$-diphenyldiazomethane grouping. The Zr1–N1 bond length [2.073 (2) Å] is well in the range described for zirconium amido complexes[13] and significantly shorter than the other two Zr2–N1 and Zr2–N2 distances [2.209 (3) and 2.255 (3) Å, respectively]. The N2–C [1.311 (3) Å] distance accounts for a normal C=N double bond, while the N1–N2 distance [1.343 (3) Å] is shorter than expected for a N–N single bond.[14] It is also remarkable that the N1–N2–C unit is

Table I. Selected Bond Distances (Å) and Angles (deg)

3		4	
Zr1–Cl1	2.502 (1)	Zr1–Cl1	2.505 (<1)
Zr1–N1	2.073 (2)	Zr1–C	2.180 (2)
Zr1–cp1	2.243	Zr1–cp1	2.194
Zr1–cp3	2.208	Zr1–cp3	2.216
Zr2–Cl2	2.517 (1)	Zr2–Cl2	2.583 (<1)
Zr2–N1	2.209 (3)	Zr2–C	2.365 (1)
Zr2–N2	2.255 (3)	Zr2–N	2.212 (1)
Zr2–cp2	2.271	Zr2–cp2	2.248
Zr2–cp4	2.248	Zr2–cp4	2.233
N1–N2	1.343 (3)	C–N	1.249 (2)
N2–C	1.311 (3)	N–C1	1.517 (2)
C–C51	1.492 (4)	C1–C2	1.512 (3)
C–C61	1.484 (4)	C1–C3	1.523 (2)
		C1–C4	1.518 (3)
Cl1–Zr1–N1	106.89 (7)	Cl1–Zr1–C	107.29 (4)
Cl1–Zr1–cp1	103.6	Cl1–Zr1–cp1	106.5
Cl1–Zr1–cp3	102.0	Cl1–Zr1–cp3	104.4
N1–Zr1–cp1	101.9	C–Zr1–cp1	95.8
N1–Zr1–cp3	109.5	C–Zr1–cp3	107.7
cp1–Zr1–cp3	131.1	cp1–Zr1–cp3	133.0
Cl2–Zr2–N1	115.82 (6)	Cl2–Zr2–C	116.42 (4)
Cl2–Zr2–N2	83.22 (6)	Cl2–Zr2–N	85.08 (4)
Cl2–Zr2–cp2	102.3	Cl2–Zr2–cp2	102.1
Cl2–Zr2–cp4	102.6	Cl2–Zr2–cp4	101.7
N1–Zr2–N2	35.01 (7)	C–Zr2–N	31.44 (5)
N1–Zr2–cp2	98.8	C–Zr2–cp2	101.1
N1–Zr2–cp4	110.8	C–Zr2–cp4	106.3
N2–Zr2–cp2	120.1	N–Zr2–cp2	112.2
N2–Zr2–cp4	108.7	N–Zr2–cp4	112.9
cp2–Zr2–cp4	127.2	cp2–Zr2–cp4	130.3
Zr1–N1–Zr2	130.5 (2)	Zr1–C–Zr2	122.1 (1)
Zr1–N1–N2	152.1 (2)	Zr1–C–N	168.0 (1)
Zr2–N1–N2	74.3 (1)	Zr2–C–N	67.5 (1)
Zr2–N2–C	149.7 (2)	Zr2–N–C1	148.2 (1)
Zr2–N2–N1	70.7 (1)	Zr2–N–C	81.0 (1)
N1–N2–C	129.1 (2)	C–N–C1	130.5 (1)
N2–C–C51	125.0 (2)	N–C1–C2	105.2 (2)
N2–C–C61	118.4 (2)	N–C1–C3	107.8 (1)
C51–C–C61	116.6 (2)	N–C1–C4	111.4 (2)

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[12] Herrmann, W. A.; Cuenca, T.; Menjõn, B.; Herdtweck, E. *Angew. Chem.* **1987**, *99*, 687; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 697. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlichtechnische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-52358, the names of the authors, and the journal citation.

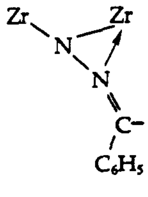
[13] Planalp, R. P.; Andersen, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 7774. Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* **1983**, *2*, 16. Bynum, R. V.; Hunter, W. E.; Rogers, R. D.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 2368. Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Abdul Malik, K. M.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010. Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030.

Table II. Fractional Atomic Coordinates and Equivalent Temperature Factors for Non-Hydrogen Atoms in Compound 3 with Estimated Standard Deviations in Parentheses[a]

atom	x	y	z	B_{eq}, Å^2
Zr1	0.36705 (1)	0.05566 (1)	0.21316 (1)	2.790 (4)
Zr2	0.24805 (1)	0.36998 (1)	0.17028 (1)	2.609 (3)
Cl1	0.25032 (4)	−0.05503 (4)	0.05089 (3)	5.41 (3)
Cl2	0.32472 (3)	0.61393 (3)	0.23418 (2)	4.28 (2)
N1	0.3952 (2)	0.2548 (2)	0.2301 (1)	2.56 (2)
N2	0.4814 (1)	0.3729 (1)	0.2463 (1)	2.37 (3)
C	0.5993 (1)	0.4325 (1)	0.3113 (1)	2.34 (5)
C11	0.1324 (1)	0.1171 (1)	0.2669 (1)	2.99 (3)
C12	0.2387 (1)	0.1158 (1)	0.3433 (1)	3.69 (3)
C13	0.2609 (1)	−0.0142 (1)	0.3346 (1)	5.09 (6)
C14	0.1688 (2)	−0.0937 (2)	0.2525 (1)	4.58 (2)
C15	0.0889 (1)	−0.0140 (1)	0.2109 (1)	4.08 (8)
C21	0.0860 (2)	0.2315 (2)	0.2462 (1)	2.93 (3)
C22	0.1247 (3)	0.3625 (3)	0.3024 (2)	3.17 (2)
C23	0.0488 (2)	0.4393 (2)	0.2570 (1)	4.31 (4)
C24	−0.0292 (2)	0.3612 (2)	0.1723 (1)	4.08 (4)
C25	−0.0044 (2)	0.2327 (2)	0.1646 (2)	3.50 (3)
C31	0.6491 (1)	0.1060 (1)	0.2333 (1)	3.66 (5)
C32	0.6180 (2)	0.0591 (2)	0.3052 (1)	3.74 (4)
C33	0.5480 (1)	−0.0728 (1)	0.2693 (1)	4.18 (7)
C34	0.5355 (2)	−0.1071 (2)	0.1771 (1)	4.55 (7)
C35	0.5969 (2)	0.0039 (2)	0.1535 (2)	4.22 (5)
C41	0.1215 (3)	0.3277 (2)	0.0064 (2)	5.54 (7)
C42	0.2221 (3)	0.4438 (3)	0.0274 (2)	6.4 (1)
C43	0.3672 (1)	0.4141 (1)	0.0453 (1)	6.69 (5)
C44	0.3477 (4)	0.2797 (4)	0.0331 (2)	6.21 (7)
C45	0.1975 (5)	0.2294 (4)	0.0113 (3)	6.10 (7)
C51	0.6557 (1)	0.3842 (1)	0.3889 (1)	2.74 (3)
C52	0.8056 (1)	0.3718 (1)	0.4103 (1)	3.61 (6)
C53	0.8592 (1)	0.3307 (1)	0.4841 (1)	4.46 (7)
C54	0.7647 (3)	0.3028 (2)	0.5374 (2)	4.84 (5)
C55	0.6170 (3)	0.3192 (2)	0.5203 (2)	4.20 (3)
C56	0.5639 (3)	0.3599 (2)	0.4456 (2)	3.24 (3)
C61	0.6814 (3)	0.5603 (2)	0.3107 (2)	2.98 (3)
C62	0.7083 (2)	0.5849 (2)	0.2325 (1)	3.89 (3)
C63	0.7895 (2)	0.7051 (2)	0.2339 (1)	4.55 (3)
C64	0.8446 (1)	0.8011 (1)	0.3146 (1)	4.85 (4)
C65	0.8209 (3)	0.7800 (2)	0.3929 (2)	4.35 (3)
C66	0.7416 (1)	0.6593 (1)	0.3917 (1)	3.53 (7)
cp1	0.1779	0.0222	0.2816	
cp2	0.0451	0.3254	0.2285	
cp3	0.5895	−0.0021	0.2276	
cp4	0.2511	0.3389	0.0247	

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter $B_{eq} = {}^4/_3[a^2\beta(1,1) + ... + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ... + bc(\cos\alpha)\beta(2,3)]$.

strongly bent [129.1 (2)°]. Other metal–ligand bond lengths are slightly longer for Zr2 than for Zr1, which can be associated with a higher electron density on the former, probably due to the η^2-coordination of the diazo ligand at Zr2. All these structural features agree with the bond formalism of A.



A

Table III. Fractional Atomic Coordinates and Equivalent Temperature Factors for Non-Hydrogen Atoms in Compound 4 with Estimated Standard Deviations in Parentheses[a]

atom	x	y	z	B_{eq}, Å^2
Zr1	0.36726 (3)	0.29167 (1)	0.18102 (1)	2.522 (4)
Zr2	0.26690 (3)	0.40118 (1)	0.37883 (1)	2.369 (3)
Cl1	0.40201 (8)	0.17745 (4)	0.27186 (4)	4.07 (1)
Cl2	0.15715 (10)	0.53202 (4)	0.43578 (4)	4.68 (2)
N	0.1733 (2)	0.4466 (1)	0.2675 (1)	2.44 (4)
C	0.2398 (3)	0.3847 (1)	0.2438 (1)	2.27 (4)
C1	0.0907 (3)	0.5129 (1)	0.2235 (2)	3.15 (5)
C2	−0.0794 (3)	0.5171 (2)	0.2561 (2)	4.81 (7)
C3	0.1853 (3)	0.5889 (2)	0.2387 (2)	4.48 (7)
C4	0.0865 (5)	0.4960 (2)	0.1373 (2)	5.87 (8)
C11	0.5849 (3)	0.3746 (1)	0.2427 (1)	2.72 (5)
C12	0.6603 (3)	0.3041 (2)	0.2182 (2)	3.55 (6)
C13	0.6534 (3)	0.3008 (2)	0.1372 (2)	4.52 (6)
C14	0.5773 (3)	0.3697 (2)	0.1105 (2)	4.27 (6)
C15	0.5347 (3)	0.4155 (2)	0.1749 (2)	3.41 (5)
C21	0.5555 (2)	0.3986 (1)	0.3232 (1)	2.53 (3)
C22	0.5525 (3)	0.3469 (1)	0.3877 (1)	2.93 (5)
C23	0.5308 (3)	0.3932 (2)	0.4551 (1)	3.41 (5)
C24	0.5173 (3)	0.4721 (2)	0.4325 (2)	3.53 (6)
C25	0.5287 (3)	0.4758 (1)	0.3510 (1)	2.94 (5)
C31	0.1281 (4)	0.2097 (2)	0.1357 (2)	5.19 (7)
C32	0.0955 (3)	0.2846 (2)	0.1144 (2)	4.05 (6)
C33	0.2095 (3)	0.3089 (2)	0.0602 (1)	4.17 (6)
C34	0.3131 (4)	0.2458 (2)	0.0467 (2)	6.48 (8)
C35	0.2596 (5)	0.1830 (2)	0.0957 (2)	7.01 (8)
C41	0.0977 (4)	0.2773 (2)	0.3756 (2)	5.08 (7)
C42	−0.0074 (4)	0.3362 (2)	0.3975 (2)	6.46 (8)
C43	0.0397 (5)	0.3614 (2)	0.4701 (2)	8.14 (9)
C44	0.1737 (5)	0.3182 (2)	0.4904 (2)	7.34 (9)
C45	0.2068 (4)	0.2676 (2)	0.4325 (2)	5.93 (8)
cp1	0.6021	0.3529	0.1766	
cp2	0.5369	0.4173	0.3899	
cp3	0.2011	0.2463	0.0905	
cp4	0.1021	0.3121	0.4332	

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter $B_{eq} = {}^4/_3[a^2\beta(1,1) + ... + c^2\beta(3,3)]$.

As the existence of a direct Zr–Zr bond in 1 has been questioned,[15] the synthesis and molecular structure of 3 seem of interest because of the relation with the behavior of a number of metal–metal-bonded complexes against diazoalkanes.[16] For instance, $N_2{=}C(CH_3)_2$ inserts into the Mo≡Mo triple bond of $[(\eta^5\text{-}C_5Me_5)Mo(CO)_2]_2$ to form $[\mu\text{-}\eta^1{:}\eta^2\text{-}N_2C(CH_3)_2][(\eta^5\text{-}C_5Me_5)Mo(CO)_2]_2$, whose molecular structure closely resembles that of 3.[16d] Diazoalkanes have also been reported to react with low-valent group 4 metallocene complexes under formal reduction to hydrazonato (2−) ligands[17] and, on the other hand, to insert into M(IV)–E bonds (ME = TiC,[18] ZrH, ZrC,[19] or ZrP[20]) giving rise to hydrazonato (1−) ligands or other related anions.

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(14) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1. Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford U.K., 1984.

(15) (a) Wielstra, Y.; Gambarotta, S.; Spek, A. L.; Smeets, W. J. J. *Organometallics* **1990**, *9*, 2142. (b) Wielstra, Y.; Meetsma, A.; Gambarotta, S.; Khan, S. *Ibid.* **1990**, *9*, 876. (c) Wielstra, Y.; Gambarotta, S.; Meetsma, A.; de Boer, J. L. *Ibid.* **1989**, *8*, 250. (d) Reference 9.

(16) (a) Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Butler, W. M.; Hay, M. S. *Organometallics* **1986**, *5*, 2283. (b) D'Errico, J. J.; Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1983**, *22*, 849. (c) Herrmann, W. A. *J. Organomet. Chem.* **1983**, *250*, 319. (d) Bell, L. K.; Herrmann, W. A.; Kriechbaum, G. W.; Pfisterer, H.; Ziegler, M. L. *Ibid.* **1982**, *240*, 381. (e) Herrmann, W. A.; Bell, L. K. *Ibid.* **1982**, *239*, C4.

(17) (a) Arvanitis, G. M.; Smegal, J.; Meier, I.; Wong, A. C. C.; Schwartz, J.; van Egen, D. *Organometallics* **1989**, *8*, 2717. (b) Arvanitis, G. M.; Schwartz, J.; van Engen, D. *Ibid.* **1986**, *5*, 2157. (c) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 7295. (d) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Ibid.* **1982**, *104*, 1918.

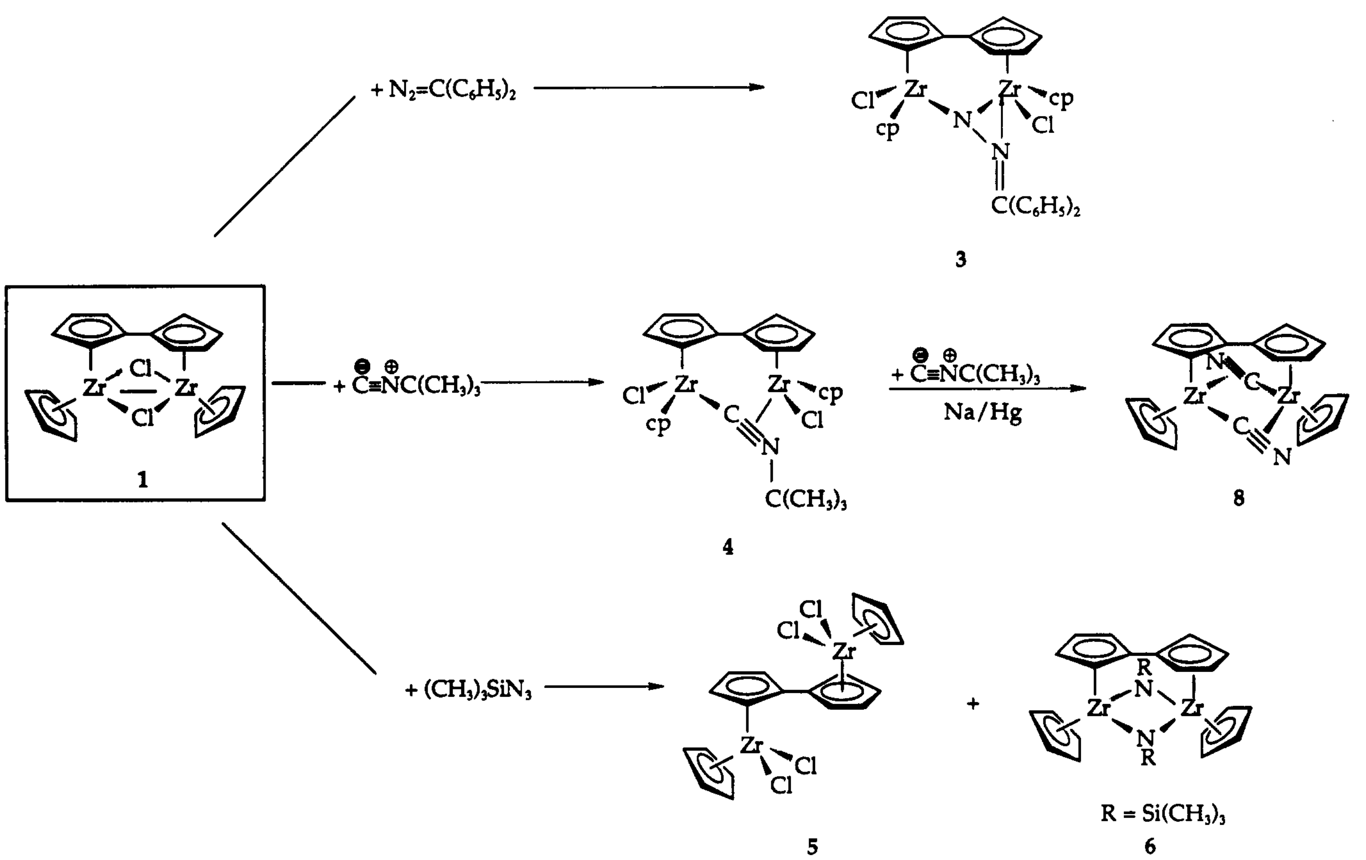
(18) Serrano, R.; Flores, J. C.; Royo, P.; Mena, M.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1989**, *8*, 1404.

(19) Gambarotta, S.; Basso-Bert, M.; Floriani, C.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1982**, 374.

(20) Hey, E.; Weller, F. *Chem. Ber.* **1988**, *121*, 1207.

(21) Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812.

Scheme I

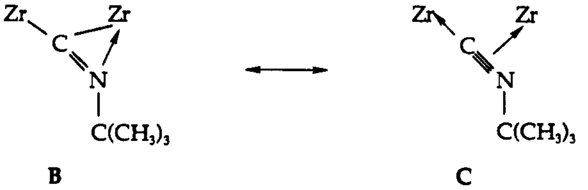


The mechanism proposed in each case depends on the nucleo- or electrophilic character of the metal center associated with its oxidation state. Thus, for Zr(IV) the attack seems to proceed through the terminal nucleophilic nitrogen $[(C_6H_5)_2C{=}N^+{=}N^-]$,[19] while for Ti(II) an associative mechanism on the electrophilic central nitrogen has been suggested to be operative.[17d]

(b) Reaction of 1 with *tert*-Butyl Isocyanide. 1 reacts in toluene solution with an equimolar amount of *tert*-butyl isocyanide at room temperature to give 4 (see Scheme I). The product is isolated as ruby red crystals in high yield (85%) and has been identified by analytical spectroscopic, and X-ray diffraction methods.

The molecular structure of 4 is shown in Figure 1b. Bond lengths, angles, and atomic positional parameters are listed in Tables I and III. The most interesting structural feature of 4 is the $\mu\text{-}\eta^1:\eta^2$ or $(\sigma + \pi)$ coordination displayed by the $CNC(CH_3)_3$ group. The Zr1–C distance [2.180 (2) Å] compares well the Zr–C(sp) bonds of $cp_2Zr(CO)_2$ [2.187 (4) Å][21] and $[(\eta^5\text{-}C_5H_4CH_3)_2Zr(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}C\text{-}(C_6H_5))]_2$ [2.188 (2) Å],[22] suggesting some degree of multiple-bond character for this interaction. The Zr2–C distance [2.365 (1) Å] is much longer. The C–N bond length [1.249 (2) Å] is longer than that observed for terminal alkyl isocyanides[23] but still shorter than a C=N double bond,[14] being in agreement with values reported for (η^2-imino-acyl)zirconium complexes.[24] The Zr1–C–N moiety is roughly linear [168.0 (1)°], while the isocyanide group is strongly bent [C–N–C1 130.5 (1)°].

According to these structural parameters, the bonding scheme for the central core of 4 can be considered as the result of the valence bond structures B and C. The ap-



pearance of a medium-intensity absorption at 1652 [1648 (sh)] cm^{-1} in the IR spectrum (KBr) can be assigned to the ν(CN) stretching mode and implies that, on coordination, an important reduction of the CN multiple-bond character has taken place. In fact, this value falls in the typical range of ν(C=N) vibrations[25] and agrees therefore with the bonding description given by formulas B and C.

Other structural features are unexceptional and very similar to those observed for 3, including the slightly longer M–ligand distances around the Zr2 atom. This fact is again related to the η^2-coordination of the isocyanide group at Zr2, which leads to an increase of electron density.

Complex 4 is to our knowledge the first example of an isocyanide group acting as a $(\sigma + \pi)$ ligand unsupported by an additional metal–metal bond.[26] As shown by NMR

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(22) (a) Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Angermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911. (b) Erker, G.; Frömberg, W.; Mynott, R.; Gabor, B.; Krüger, C. *Angew. Chem.* **1986**, *98*, 456; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 463. (c) Cf. also the very short distance [2.194 (7) Å] reported for $[\mu\text{-}CH{=}CH(C_6H_5)](\mu\text{-}Cl)(cp_2Zr)_2$ and ascribed to some metal-carbene bond character: Erker, G.; Kropp, K.; Arwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1555.

(23) C≡N bond distances of about 1.14 Å have been reported for $CNC(CH_3)_3$ adducts of $TiCl_4$ and VCl_3: Carofiglio, T.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1989**, *28*, 4417. Cf. also: Jones, W.; Duttweiler, R. P., Jr.; Feher, F. J. *Ibid.* **1990**, *29*, 1505.

(24) Erker, G.; Zwettler, R.; Krüger, C. *Chem. Ber.* **1989**, *122*, 1377 and references therein.

(25) Pretsch, E.; Seibl, J.; Simon, W.; Clerc, T. *Tabellen zur Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden*, 3rd ed.; Springer-Verlag: Berlin, 1986.

spectroscopy this structure is also maintained in [D_8]-toluene solution. At room temperature, both ^1H and ^{13}C NMR spectra show two very intense, sharp singlets (^1H δ = 6.21, 5.81 ppm; ^{13}C δ = 110.89, 119.34 ppm) as expected for two inequivalent cp groups. The eight multiplets observed between 4.5 and 6.5 ppm in its ^1H NMR spectrum as well as the ten small signals in the 90–125 ppm region of its ^{13}C NMR spectrum can be assigned to a fulvalene group with no elements of symmetry. The remainder resonances are due to the isocyanide ligand.

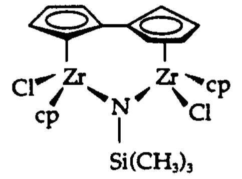
Isocyanides are known to typically insert into M–M bonds of either single[27] or multiple[26a,e] character. Complex 4 can therefore be considered as arising from a simple isocyanide insertion into a Zr–Zr bond. The real existence of such a direct intermetallic interaction cannot, however, be easily ascertained. In our original synthesis of 1, we suggested a Zr–Zr bond to be operative in the complex in order to account for its diamagnetism.[6a] Subsequently, the intermetallic distance [Zr–Zr 3.233 (1) Å] was also found to be consistent with this assumption.[6c] Unfortunately, in polynuclear complexes containing ancillary bridging ligands, neither their magnetic properties nor the intermetallic distances provide per se enough evidence to conclude whether a M–M bond does actually exist.[28] In this type of complex, diamagnetism can, in fact, be due to spin-pairing through the bridging system[29] and short M–M distances can result from certain geometrical requirements of the bridging ligands.[30] Under these circumstances, the "chemical significance" of a hypothetical M–M bond becomes more important.[31] Since 1 not only is diamagnetic and has an adequate Zr–Zr distance but also reacts with diphenyldiazomethane and *tert*-butyl isocyanide as typical M–M bond-containing species do, it is tempting to assume that 1 does actually contain a Zr(III)–Zr(III) bond.

(c) Reaction of 1 with Trimethylsilyl Azide. 1 reacts with equimolar amounts of trimethylsilyl azide in boiling THF as illustrated in Scheme I. The initially deep violet solution first turns green and then orange; a yellow solid gradually precipitates. The solid was identified by elemental analyses and IR spectroscopy as the known zirconium(IV) complex (μ-η^5:η^5-$C_{10}H_8$)[(η^5-C_5H_5)$ZrCl_2$]$_2$ (5).[12] 5 is rather insoluble in the usual organic solvents so it can be separated by simple filtration. By evaporation of the filtrate, an orange residue is obtained, which can further be purified by means of sublimation in vacuo. Eventually, 6 was obtained as orange needles in good yields (75%).

We formulate 6 as (μ-η^5:η^5-fulvalene)bis[μ-(trimethylsilyl)imido]bis[(η^5-cyclopentadienyl)zirconium] (see Scheme I) depending on analytical results and on mass, IR, and ^1H and ^{13}C NMR spectrometry. Bi- and oligonuclear μ-imido complexes are not uncommon in group 4 metal chemistry.[32] Only recently, Bergman[33] and Wolczanski[34] have reported the syntheses of extremely reactive terminal imido complexes of Zr, which in the absence of an adequate trapping ligand tend to dimerize.[33]

As expected for the C_{2v} symmetrical arrangement depicted in Scheme I, the ^1H and ^{13}C NMR spectra of 6 (C_6D_6, room temperature) show two very intense, sharp single resonances attributable to the cyclopentadienyl (^1H δ = 6.01 ppm; ^{13}C δ = 110.8 ppm) and (trimethylsilyl)imido (^1H δ = –0.08 ppm; ^{13}C δ = 6.9 ppm) groups, respectively. In addition, the fulvalene ligand gives rise to three signals in the ^{13}C NMR spectrum (δ = 116.3, 115.1, 106.0 ppm) and two triplets in the ^1H NMR spectrum [δ = 5.77, 5.63 ppm; J(H,H) = 2.93 Hz] also in agreement with the assumed geometry. The appearance of a strong absorption at 1245 [1258 (sh)] cm^{-1} in the IR spectrum of 6 (KBr) can be assigned to the δ(SiMe) vibration mode characteristic of trimethylsilyl derivatives.[25]

Like other low-valent group 4 metal derivatives,[35] 1 reacts with Me_3SiN_3 under oxidation of the metal center and formation of a μ-imido complex. The products obtained could nonetheless be considered as the result of a three step process: (1) interaction of the metal complex with the organic azide to give a metal azide intermediate,[36] (2) loss of molecular nitrogen rendering the single-bridged μ-imido complex 7 (isoelectronic with 2), and (3) intermolecular ligand exchange, eventually yielding the mixture 5 + 6. This latter step could be favored by the low solubility of 5. Attempts to isolate and characterize 7 by carrying out the reaction under milder conditions have not been succesful.[37]



7

(d) Reaction of 4 with *tert*-Butyl Isocyanide under Reductive Conditions. Upon treatment of an equimolar mixture of 4 and *tert*-butyl isocyanide with an excess of 1% sodium amalgam in refluxing toluene, the initially deep violet solution turns orange in color. From this solution complex 8 is isolated as an orange, crystalline solid (77% yield) according to Scheme I. 8 has been characterized by means of analytical and spectroscopic methods.

The ^1H and ^{13}C NMR spectra of 8 show no high-field resonances characteristic of alkyl groups.[25] The low-intensity signal observed at δ = 201.09 ppm in its ^{13}C NMR spectrum can be assigned to the cyanide carbon. The absence in its IR spectrum of any absorptions above 2000 cm^{-1}—characteristic of terminal or bridging (M—CN—M′) cyanides[38]—together with the appearance of a sharp, very strong band at 1869 cm^{-1} would agree with a (σ + π) coordination of the cyanide anion. This type of coordination, though unusual, has already been documented in several

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(26) (a) Adams, H.; Bailey, N. A.; Bannister, C.; Faers, M. A.; Fedorko, P.; Osborn, V. A.; Winter, M. J. *J. Chem. Soc., Dalton Trans.* **1987**, 341. (b) Deeming, A. J.; Donovan-Mtunzi, S. *J. Chem. Soc., Dalton Trans.* **1985**, 1609. (c) Bernal, I.; Brunner, H.; Wachter, J. *J. Organomet. Chem.* **1984**, *277*, 395. (d) Brunner, H.; Buchner, H.; Wachter, J.; Bernal, I.; Ries, W. H. *Ibid.* **1983**, *244*, 247. (e) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *Organometallics* **1982**, *1*, 231. (f) Benner, L. S.; Olmstead, M. M.; Balch, A. L. *J. Organomet. Chem.* **1978**, *159*, 289. (g) Cf. also: Deeming, A. J.; Donovan-Mtunzi, S. *Organometallics* **1985**, *4*, 693.

(27) Usón, R.; Forniés, J.; Espinet, P.; Martínez, F.; Fortuño, C.; Menjón, B. *J. Organomet. Chem.* **1983**, *256*, 365. Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099. Olmstead, M.; Hope, H.; Benner, L. S.; Balch, A. L. *Ibid.* **1977**, *99*, 5502.

(28) Baird, M. C. *Prog. Inorg. Chem.* **1968**, *9*, 1.

(29) Gerloch, M. *Prog. Inorg. Chem.* **1979**, *26*, 1.

(30) It is astonishing, for instance, that the Zr–Zr distance reported for the binuclear d^0 complex (μ-$NSiMe_3$)[cp Zr(η^1:η^5-C_5H_4)]$_2$ is as short as 3.073 (1) Å. See ref 15b.

(31) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; p 1052.

(32) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. See also ref 30.

(33) Walsh, P. J.; Hollander, F. J.; Bergman, R. G *J. Am. Chem. Soc.* **1988**, *110*, 8729.

(34) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.

(35) Coutts, R. S. P.; Surtees, J. R. *Aust. J. Chem.* **1966**, *19*, 387. See also ref 15b.

(36) Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1025.

(37) The intermediacy of 7 could account for the initial change in the color of the reaction medium (from deep violet to green).

(38) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., John Wiley & Sons: New York, 1986; p 272.

cases.[39] Only for $[Rh_2(\mu\text{-}CN)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ [dppm = bis(diphenylphosphino)methane],[39a] has the ν(CN) been assigned and reported to appear at 2044 cm^{-1} as a weak absorption. The dramatic lowering in the ν(CN) observed for complex 8 could suggest the existence of intensive metal–ligand π-interaction. Attending to the isoelectronic relationship $C{\equiv}N^- \triangleq C{\equiv}CR^-$, meaningful comparisons between the spectroscopic properties of 8 and that exhibited by a number of known $\mu\text{-}\eta^1{:}\eta^2$-alkynyl complexes of Ti(III)[40] and Zr(III)[22a,b] of formula $[(\mu\text{-}\eta^1{:}\eta^2\text{-}C^{\alpha}{\equiv}C^{\beta}R)Mcp_2]_2$ can be drawn. In the latter, the C^{α} resonance typically appears in the 200–230 ppm region and the ν(C≡C) vibration mode is usually assigned to medium-to-weak absorptions around 1800 cm^{-1}, which involves a decrease of about 200 cm^{-1} relative to their σ-alkynyl analogues, $cp_2M^{IV}(C_2R)_2$.[22a,b,40] The ^1H NMR spectrum of 8 shows only one singlet (δ = 5.82 ppm) and four multiplets (δ = 6.16, 5.10, 4.92, 4.28 ppm) assignable to the cp and fulvalene groups respectively. The resonance pattern originated by the fulvalene ligand suggests that, differing from the dynamic behavior exhibited by the $\mu\text{-}\eta^1{:}\eta^2$-alkynyl derivatives of Zr(III)[22a,b] and all known $\mu\text{-}\eta^1{:}\eta^2$-cyano metal complexes,[39] 8 is a conformationally stable molecule in solution at room temperature. Accordingly, its ^{13}C NMR spectrum shows one cp signal (δ = 103.8 ppm) and five small resonances due to the $C_{10}H_8$ group (δ = 111.0, 105.6, 100.6, 99.8, 96.3 ppm).

As illustrated in Scheme I, the preceeding reaction involves the dealkylation of the isocyanide ligand. This kind of reaction has been reported to occur in a number of (predominantly cationic) isocyanide complexes of Mo, W,[41] Tc, Re,[42] Ru, Os,[43] and Pt,[44] as well as by interaction of the free isocyanide with powerful reducing agents such as cp^*_2V ($cp^* = \eta^5\text{-}C_5Me_5$),[45] $cp^*_2Sm(THF)_2$,[46] and *trans*-$Mo(N_2)_2(Me_8[16]aneS_4)$.[47] Alkali- or alkaline-earth-metal solutions exhibit the same effect.[48]

In order to determine the fate of the organic leaving group, we performed a GC analysis of the gas phase in the reaction mixture. It showed the presence of almost equimolar amounts of $(CH_3)_3CH$ and $(CH_3)_2C{=}CH_2$, i.e. the products expected for the disproportionation of the $(CH_3)_3C^{\bullet}$ radical.[49] The reaction, however, is not likely to proceed via free alkyl radicals. As a test to establish whether the Zr metal complex was actually involved in effecting the reductive cleavage of the C—N bond, we reacted $CNC(CH_3)_3$ with sodium amalgam in refluxing toluene under exactly the same conditions and found no traces of $(CH_3)_3CH$ or $(CH_3)_2C{=}CH_2$.

The response of 4 to reductive treatment markedly contrasts with the behavior of cp_2ZrCl_2 under similar conditions. Thus, the latter is known to react with 2,6-dimethylphenyl isocyanide ($CN\text{-}2,6\text{-}C_6H_3Me_2$) in the presence of magnesium turnings affording $cp_2Zr(CN\text{-}2,6\text{-}C_6H_3Me_2)_2$.[50] No dealkylation was observed in this case nor in the synthesis of the analogous complex $cp^*_2Zr(CN\text{-}2,6\text{-}C_6H_3Me_2)_2$.[51] As *end-on*-coordinated isocyanides are obviously able to stabilize divalent Zr complexes, this striking difference could be attributed to the initial ($\sigma + \pi$) coordination of the isocyanide group in 4, possibly resulting in additional activation of the ligand. Interestingly, the fact that alkyl isocyanides, CNR (R = C_2H_5, $n\text{-}C_3H_7$, C_4H_7, $n\text{-}C_4H_9$), react with bare Fe^+ in the gas phase under cleavage of the CN—R bond has been rationalized by Schwarz et al. assuming an initial *side-on* coordination of the C≡N functionality to the metal ion, followed by δ-(C—H) activation and final β(C—N) cleavage.[52] Jones and Kosar have also suggested a δ-elimination process as a likely step in the dealkylation of $CNC(CH_3)_3$ by thermolysis in the presence of $(DMPE)_2Ru(naphthyl)H$ [DMPE = bis(dimethylphosphino)ethane].[43a]

8 is the first reported organozirconium cyano complex. There are, in fact, surprisingly few Zr cyano compounds in general.[53] The only ones so far isolated and described in some detail are $M_5[Zr^0(CN)_5]$ (M = K, Rb),[54] $K_2[Zr^{II}(CN)_4]$,[55] and $Zr^{IV}(CN)_2Br_2$.[56]

Conclusion

All reactions reported in this paper proceed in good yields and represent a typical piece of organozirconium(III) chemistry. In all three cases, the fulvalene ligand maintains its stable bridging function, while the chloro ligands invariably split up, thereby incorporating the incoming organic fragment. The chemical behavior of 1 both against diphenyldiazomethane and *tert*-butyl isocyanide lends further support to the existence of a metal–metal bond in the starting material 1, as was first suggested by us to account for its diamagnetism[6a] and the short Zr–Zr distance [3.233 (1) Å].[6c]

Experimental Section

General Procedures and Materials. All reactions were performed under an inert-gas atmosphere (dry nitrogen) by using standard Schlenk techniques. Solvents were dried over sodium wire and freshly distilled under nitrogen prior to use. A glovebox, Braun MB-200, was used to weigh air-sensitive solids and to prepare samples for IR and NMR measurements. Deuterated solvents, $CDCl_3$ and CD_2Cl_2 were treated with P_4O_{10} (Sika-

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(39) (a) Deraniyagala, S. P.; Grundy, K. R. *Inorg. Chim. Acta* **1984**, *84*, 205. (b) Aspinall, H. C.; Deeming, A. J.; Donovan-Mtunzi, S. *J. Chem. Soc., Dalton Trans.* **1983**, 2669. (c) Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096. (d) Curtis, M. D.; Klingler, R. J. *J. Organomet. Chem.* **1978**, *161*, 23.

(40) Wood, G. L.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1989**, *28*, 382.

(41) Bell, A.; Walton, R. A. *J. Organomet. Chem.* **1984**, *263*, 359. Bell, A.; Lippard, S. J.; Roberts, M.; Walton, R. A. *Organometallics* **1983**, *2*, 1562. Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 1263. Giandomenico, C. M.; Hanau, L. H.; Lippard, S. J. *Organometallics* **1982**, *1*, 142. Caravana, C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1982**, *21*, 1860. Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Ibid.* **1981**, *20*, 4069.

(42) Farr, J. P.; Abrams, M. J.; Costello, C. E.; Davidson, A.; Lippard, S. J.; Jones, A. G. *Organometallics* **1985**, *4*, 139.

(43) (a) Jones, W. D.; Kosar, W. P. *Organometallics* **1986**, *5*, 1823. (b) Tetrick, S. M.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 3363.

(44) Crociani, B.; Nicolini, M.; Richards, R. L. *Inorg. Chim. Acta* **1975**, *12*, 53. Treichel, P. M.; Wagner, K. P.; Hess, R. W. *Inorg. Chem.* **1973**, *12*, 1471. Treichel, P. M.; Hess, R. W. *J. Chem. Soc., Chem. Commun.* **1970**, 1626. Yamamoto, Y.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1873. Tschugaeff, L.; Teearu, P. *Ber. Dtsch. Chem. Ges.* **1914**, *47*, 2643.

(45) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1984**, *23*, 1739.

(46) Evans, W. J.; Drummond, D. K. *Organometallics* **1988**, *7*, 797.

(47) Adachi, T.; Sasaki, N.; Ueda, T.; Kaminaka, M.; Yoshida, T. *J. Chem. Soc., Chem. Commun.* **1989**, 1320. $Me_8[16]aneS_4$ = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane.

(48) Niznik, G. E.; Walborsky, H. *J. Org. Chem.* **1978**, *43*, 2397. Büchner, W.; Dufaux, R. *Helv. Chim. Acta* **1966**, *49*, 1145. Ugi, I.; Bodesheim, F. *Chem. Ber.* **1961**, *94*, 1157.

(49) Tsang, W. *J. Am. Chem. Soc.* **1985**, *107*, 2872.

(50) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Engelhardt, H. E.; Herberhold, M. *J. Organomet. Chem.* **1986**, *317*, C38.

(51) Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6450. See also: Kool, L. B.; Rausch, M. D.; Herberhold, M.; Alt, H. G.; Thewalt, U.; Honodl, B. *Organometallics* **1986**, *5*, 2465.

(52) Eller, K.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 3068.

(53) Fay R. C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 3, p 363. Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*; Academic Press: London, 1976.

(54) Nicholls, D.; Ryan, T. A. *Inorg. Chim. Acta* **1977**, *21*, L17.

(55) Dodsworth, E. S.; Eaton, J. P.; Ellerby, M. P.; Nicholls, D. *Inorg. Chim. Acta* **1984**, *89*, 143.

(56) Boyle, E. L.; Dodsworth, E. S.; Nicholls, D.; Ryan, T. A. *Inorg. Chim. Acta* **1985**, *100*, 281.

pent/Merck) and [D_8]tetrahydrofuran over sodium/potassium alloy, then distilled, and stored under nitrogen. The following spectrometers were used: NMR, Jeol JMX-GX-270; IR, Nicolet FT-5DX and Beckman 4240; MS, Varian MAT 311-A. Elemental analyses were carried out in our microanalytical laboratory. Starting materials $(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\mu\text{-Cl})Zr(\eta^5\text{-}C_5H_5)]_2$[6a] and $N_2C(C_6H_5)_2$[57] were prepared according to literature methods. $CNC(CH_3)_3$ and $(CH_3)_3SiN_3$ were purchased from Aldrich and used as received.

(μ-η^1:η^2-Diphenyldiazomethane)(μ-η^5:η^5-fulvalene)bis[chloro(η^5-cyclopentadienyl)zirconium] (3). The addition of a little excess of diphenyldiazomethane (0.3 g, 1.5 mmol) to a deep violet solution of 1 (0.5 g, 0.98 mmol) in toluene (50 mL) at 70 °C caused its color to immediately turn bright red. After 1 h of stirring, the solution was dried under vacuum and the remaining residue washed with *n*-hexane (3 × 10 mL) to eliminate the excess of diphenyldiazomethane. Recrystallization from toluene rendered 3 as orange crystals (0.45 g, 65% yield). IR (cm^{-1}, KBr): 1490, 1479, 1443, 1205, 1097, 1068, 1025, 1013, 836, 820, 810, 810, 696, 435. Anal. Found (calcd) for $C_{33}H_{28}N_2Cl_2Zr_2$: C, 55.9 (56.1); H, 4.0 (4.0); N, 3.9 (4.0).

(μ-η^1:η^2-*tert*-Butyl isocyanide)(μ-η^5:η^5-fulvalene)bis[chloro(η^5-cyclopentadienyl)zirconium] (4). A toluene (70 mL) solution of 1 (0.5 g, 0.98 mmol) was treated with an equimolar amount of *tert*-butyl isocyanide (110 μL, 0.98 mmol). The deep violet solution turned immediately red. After filtration, the solution was dried under vacuum and the residue washed with *n*-hexane (2 × 10 mL) and diethyl ether (2 × 5 mL). The remaining ruby red powder was identified as 4 (0.49 g, 85% yield). 270-MHz ^1H NMR ([D_8]tetrahydrofuran): $\delta = 6.47$, 6.34, 6.21, 6.01, 5.69, 5.54, 5.06, 4.88 (8 m, 8 H, $C_{10}H_8$), 6.21, 5.81 (2 s, 5 H each, C_5H_5), 1.49 (s, 9 H, CH_3). 67.8-MHz ^{13}C NMR ([D_8]tetrahydrofuran): $\delta = 218.12$ (CN), 125.67, 118.22, 114.83, 112.43, 104.75, 103.37, 103.32, 102.91, 100.37, 94.54 ($C_{10}H_8$), 110.89, 110.32 (C_5H_5), 30.82 [$C(CH_3)_3$], 29.93 (CH_3). IR (cm^{-1}, KBr): 1652/1648 (sh) (CN). EI-MS (70 eV): *m/e* 534 ($[M - C(CH_3)_3]^+$). Anal. Found (calcd) for $C_{25}H_{27}NCl_2Zr_2$: C, 51.0 (50.5); H, 4.7 (4.6); N, 2.2 (2.3).

Reaction of 1 with $(CH_3)_3SiN_3$. To a deep violet solution of 1 (1 g, 1.95 mmol) in THF (50 mL) was added $(CH_3)_3SiN_3$ (257 μL, 1.95 mmol) and the mixture refluxed for 7 h. During this time, the solution turned first green and then changed into a suspension of a yellow solid in an orange solution. After cooling, the yellow solid was separated by filtration and identified as **5** by IR spectroscopy and elemental analyses (0.52 g, 91% yield). The filtrate was evaporated to dryness and the resulting residue was purified by sublimation. At 150 °C/10^{-3} Torr, **6** sublimed as deep orange needles (0.45 g, 75% yield). 270-MHz ^1H NMR ([D_8]toluene): $\delta = 6.01$ (s, 10 H, C_5H_5), 5.77, 5.63 (2 t, 8 H, $C_{10}H_8$; $J(H,H) = 2.93$ Hz), -0.08 (s, 18 H, CH_3). 67.8-MHz ^{13}C NMR ([D_8]toluene): $\delta = 116.3$ (C1), 115.1, 106.0 (C2, C3), 110.8 (C_5H_5), 6.9 (CH_3). IR (cm^{-1}, KBr): 1258 (m), 1245 (s) [$\delta(SiMe_3)$]. EI-MS (70 eV): *m/e* 612 (M^+), 597 ($[M - CH_3]^+$), 547 ($[M - C_5H_5]^+$). Anal. Found (calcd) for $C_{26}H_{36}N_2Si_2Zr_2$: C, 50.4 (50.7); H, 6.1 (5.9); N, 3.5 (4.5).

Bis(μ-η^1:η^2-cyano)(μ-η^5:η^5-fulvalene)bis[(η^5-cyclopentadienyl)zirconium] (8). A toluene (70 mL) solution of 4 (0.58 g, 0.98 mmol) and an equimolar amount of *tert*-butyl isocyanide (110 μL, 0.98 mmol) was treated with an excess of 1% sodium amalgam (approximately 70 mg of Na, 3 mmol) and refluxed for 5 h. After cooling, the solution was filtered off and the filtrate evaporated to dryness. Recrystallization of the obtained residue from toluene/*n*-hexane rendered 8 as orange crystals (0.37 g, 77% yield). 270-MHz ^1H NMR (CD_2Cl_2): $\delta =$ 6.16, 5.10, 4.92, 4.28 (4 m, 2 H each, $C_{10}H_8$), 5.82 (s, 10 H, C_5H_5). 67.8-MHz ^{13}C NMR (CD_2Cl_2): $\delta = 201.09$ (CN), 111.0, 105.6, 100.6, 99.8, 96.3 ($C_{10}H_8$), 103.8 (C_5H_5). IR (cm^{-1}, KBr): 1869 (CN). EI-MS (70 eV): *m/e* 490 (M^+). Anal. Found (calcd) for $C_{22}H_{18}N_2Zr_2$: C, 53.7 (53.6); H, 3.7 (3.7); N, 5.6 (5.7).

Identification of the Gas Mixture. A one-fifth scale, separate reaction was performed as described above in a sealed flask. A sample of the gas chamber was chromatographed by using a Al_2O_3 column and shown to contain an almost equimolar amount of 2-methylpropane and 2-methylprop-1-ene.

Table IV. Summary of Crystal Data and Details of Intensity Collection and Refinement

	3	4
formula	$C_{33}H_{28}Cl_2N_2Zr_2$	$C_{25}H_{27}Cl_2NZr_2$
fw	705.9	594.8
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$ (IT No. 2)	$P2_12_12_1$ (IT No. 19)[a]
conditions		$h00$, $0k0$, $00l$; $hkl = 2n$
cryst dimens, mm	0.20 × 0.20 × 0.10	0.30 × 0.20 × 0.05
cryst color and habit	orange prisms	ruby red plates
temp, K	296	296
a, Å	9.189 (1)	8.233 (1)
b, Å	10.808 (1)	16.891 (2)
c, Å	15.833 (1)	17.312 (2)
α, deg	104.93 (1)	
β, deg	100.35 (1)	
γ, deg	97.82 (1)	
V, Å^3	1467	2407
Z	2	4
d_{calc}, g cm^{-3}	1.598	1.641
μ(Mo Kα), cm^{-1}	9.1	10.9
scan type	ω-scan	ω-scan
scan time, s	max 90	max 60
scan width, deg	$(0.80 + 0.30 \tan\theta)$	$(0.80 + 0.30 \tan\theta)$
$2\theta_{max}$, deg/octants	$45/\pm h,\pm k,\pm l$	$50/\pm h,+k,+l$
bckgrd	25% additional scan at each end of scan	
corrns	LP; 10% decay	LP; empirical absorpn (T: 0.8008–1.000)
no. of reflns collcd	7537	4517
R_{merge} on $\lvert F_o\rvert$	0.027	0.011
no. of unique data	3774	4205
no. of reflns incl (NV)	3329 [$I > 1.0\sigma(I)$]	4029 [$I > 1.0\sigma(I)$]
no. of variables (NO)	352	271
data:variable ratio	9.5	14.9
R^b	0.035	0.017
R_w	0.026	0.018
GOF/p	1.947/0.00	2.212/0.00
weighting scheme, w	$1/\sigma(F_o)^2$	$1/\sigma(F_o)^2$
largest shift/err	<0.01	<0.01
max/min, e_o^-/Å^3	+0.37/−0.40	+0.39/−0.36

[a] A test for chirality yields hardly poorer agreement factors ($R = R_w = 0.018$). [b] $R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$, $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$ and GOF $= [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(NO - NV)]^{1/2}$.

X-ray Crystal Structure Analysis of $C_{33}H_{28}Cl_2N_2Zr_2$ (3) and $C_{25}H_{27}Cl_2NZr_2$ (4). Both measurements were performed on an Enraf-Nonius CAD-4 diffractometer (Mo Kα radiation λ = 71.073 pm; incident beam graphite monochromater; ω-scans). Unit-cell parameters were derived from the diffractometer setting angles for 30 reflections (35° < θ < 49°) widely separated in reciprocal space. Lorentz, polarization, and if necessary an absorption correction and a correction for decay were applied to the data. The crystal structure was solved by direct methods. Approximate positions for the non-hydrogen atoms were obtained from an E map. Hydrogen atoms were included at their calculated positions in the final rounds of full-matrix least-squares refinement of all non-hydrogen atom positional and anisotropic temperature factor parameters. Crystallographic calculations were performed on Vax 3100 and Vax 730 computers by use of the STRUX-III system incorporating SHELX-76 and the Enraf-Nonius Structure Determination Package and the direct-methods programs MULTAN 11/82 and SHELX-86. Neutral-atom scattering factors as well as anomalous dispersion factors used in the structure factor calculations were taken from refs 61 and 62. In the full-matrix least-squares

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(57) Smith, L. I.; Howard, K. L. In *Organic Synthesis*; John Wiley & Sons: New York, 1955; Collect. Vol. 3, p 351.

(58) Sheldrick, G. M. SHELXS-86. In *Crystallographic Computing 3*; Sheldrick, G. M.; Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1986; pp 175–189.

(59) XRAY76-SYSTEM, program PARAM, computer adaptation by M. Birkhahn, University of Marburg 1979; and E. Herdtweck, Technical University of Munich, 1986.

(60) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; German, G.; Declercq, J.-P.; Woolfson, M. M. Multan 11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Universities of York and Louvain, 1982.

(61) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2B.

(62) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press, Birmingham, U.K., 1974; Vol. IV, Table 2.3.1.

iterations, $\sum w\Delta^2[w = 1/\sigma(F_0)^2, \Delta = (|F_0| - |F_c|)]$ was minimized. Bond lengths and angles are listed in Table I. Tables II and III represent the atomic coordinates. Further details of data collection and refinement are represented in Table IV.[58-65]

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Note Added in Proof. After submission of this paper, extended Hückel calculations on a series of binuclear complexes of Zr(III) exhibiting Zr–Zr distances ranging from 3.05 to 4.25 Å were carried out. These calculations suggest the existence of "a substantial amount of through-space metal–metal interaction at distances larger than 3.5 Å". This conclusion strongly supports ours, thereby reinforcing it.[66]

Supplementary Material Available: For 3 and 4, lists of bond lengths and angles, least-squares planes, atomic fractional coordinates, and thermal parameters and ORTEP stereo plots (35 pages); listings of observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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(63) Kiprof, P.; Herdtweck, E.; Schmidt, R. E.; Birkhahn, M.; Massa, W. STRUX-II. A System of Computer Programs To Handle X-ray Diffraction Data, Technische Universität München, 1987, and Universität Marburg, 1978.

(64) Frenz, B. A. *ENRAF-NONIUS SDP-Plus Structure Determination Package*, version 4.0; Enraf-Nonius: Delft, Holland, 1988.

(65) Keller, E. SCHAKAL. A Plot Program for Crystal Structure Illustrations. University of Freiburg, 1988.

(66) Rohmer, M.-M.; Bènard, M. *Organometallics* **1991**, *10*, 157.

Novel Organometallic Complexes Containing Aromatic Azines: Synthesis and X-ray Crystal Structure of 4,6-Bis[(η^5-cyclopentadienyl)dicarbonyliron] 2-(Methylthio)pyrimidine[1]

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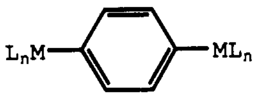
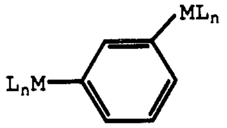
The syntheses of 13 monometallic and 4 bimetallic complexes in which $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, Fp, groups are bound to substituted pyridine, pyrazine, pyridazine, and pyrimidine rings is described. These species are prepared by metathesis reactions between the appropriate number of equivalents of NaFp and the chloro- or fluoro-substituted azine precursors in 25–95% yields and structural factors affecting these yields are discussed. These new materials have been fully characterized by conventional spectroscopic techniques and are shown to contain Fe–C σ-bonds. The X-ray crystal structure of the title complex ($C_{19}H_{14}Fe_2N_2O_4$; a = 11.119 (2) Å, b = 11.553 (3) Å, c = 15.769 (2) Å, β = 104.49 (1)°, V = 1960 Å^3; monoclinic; $P2_1/n$; Z = 4) confirms that it has the expected structure about the pyrimidine ring. It also reveals that, contrary to expectations from frontier molecular orbital theory, the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ group shows a preference for orientations in which its mirror plane is perpendicular to that of the pyrimidine ring. The spectroscopic data provide no evidence for the existence of any electronic interaction between the metal centers of the new bimetallic azine bridged complexes having meta substitution geometries.

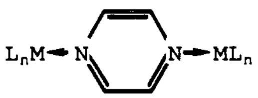
Introduction

Work in our laboratories has recently been directed toward the investigation of the nature and degree of the long-range indirect metal–metal interaction in complexes in which two or more metal centers are bridged by arene rings.[1-3] In these species, both metals are directly σ-bonded to the arene carbon, generally in either a 1,3 or 1,4 fashion, e.g.





(where ML$_n$ = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, $Mn(CO)_5$, etc.). Other workers have reported related studies in which the phenylene bridges in these complexes are formally replaced by heterocyclic ring(s) (e.g. pyrazine, 4,4′-bipyridine, etc.) and where either both metals are bonded to the ring nitrogen atoms by formal nitrogen to metal dative bonds, e.g.[4]



(where ML$_n$ = a large variety of 16-electron metal centers) or where the metal centers are bonded by both metal–

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(1) (a) Organometallic Complexes with Electronic Bridges. 6. For part 5 see ref 2e. (b) Taken in part from: Chukwu, R. M.Sc. Thesis, The University of Alberta, 1990. Parts of this work have been presented orally: (c) Chukwu, R.; Hunter, A. D. 72nd Canadian Chemical Conference, Victoria, BC, June 1989; Abstract 348. (d) Chukwu, R.; Hunter, A. D. 73rd Canadian Chemical Conference, Halifax, NS, July 1990; Abstract 623IN-F14.

(2) (a) Richter-Addo, G. B.; Hunter, A. D. *Inorg. Chem.* **1989**, *28*, 4063–4065. (b) Hunter, A. D. *Organometallics* **1989**, *8*, 1118–1120. (c) Hunter, A. D.; Szigety, A. B. *Organometallics* **1989**, *8*, 2670–2679. (d) Hunter, A. D.; McLernon, J. L. *Organometallics* **1989**, *8*, 2679–2688. (e) Richter-Addo, G. B.; Hunter, A. D.; Wichrowska, N. *Can. J. Chem.* **1990**, *68*, 41–48.

(3) (a) Hunter, A. D.; Chukwu, R.; Mozol, V.; Ristic-Petrovic, D. 200th National Meeting of the American Chemical Society, Washington, DC, Aug 1990; INOR 121. (b) Hunter, A. D.; Mozol, V. Santarsiero, B. D. 73rd Canadian Chemical Conference, Halifax, NS, July 1990; Abstract 614 IN-F14.

(4) See for example: (a) Woitellier, S.; Launay, J. P.; Spangler, C. W. *Inorg. Chem.* **1989**, *28*, 758–762. (b) Gross, R.; Kaim, W. *Inorg. Chem.* **1986**, *25*, 498–506. (c) Zulu, M. M.; Lees, A. J. *Organometallics* **1989**, *8*, 955–960.

0276-7333/91/2310-2141$02.50/0