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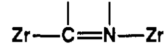
# Synthesis of Pyridine Complexes of Zirconium(III) Chloride and the Apparent Oxidation to Zirconium(IV) by a Nitrile

Although zirconium(III) halides have been known since 1923,[1] it was not until the late 1960s that the first ligand adducts were prepared by Fowles and co-workers.[2] These early complexes were prepared by reacting zirconium(III) halides (synthesized by high-temperature synthetic procedures) with nitrogen-based ligands such as pyridine and acetonitrile (eqs 1 and 2). Dinuclear

$$ZrX_3 + \text{excess pyridine} \xrightarrow{\text{3-5 days}} ZrX_3(py)_2 \tag{1}$$

$$2ZrX_3 + \text{excess } CH_3CN \xrightarrow{\text{3-5 days}} Zr_2X_6(CH_3CN)_5 \tag{2}$$

structures with the pyridine or acetonitrile ligands bound through nitrogen were proposed for the compounds on the basis of their low magnetic moments, chemical composition, and other spectroscopic data, but no definitive structural characterization was reported. For the acetonitrile complexes a structure with the linkage shown in I was also discussed.



$$Zr{-}\overset{\overset{\displaystyle Me}{|}}{C}{=}\overset{\overset{\displaystyle X}{|}}{N}{-}Zr$$

I

In 1981 Wengrovius and Schrock reported a general synthesis for phosphine complexes of zirconium(III) involving the reduction of $ZrCl_4$ with sodium amalgam in the presence of phosphine (eq 3).[3] This procedure produced the first structurally characterized

$$2ZrCl_4 + 2Na/Hg + 4PR_3 \rightarrow [ZrCl_3(PR_3)_2]_2 + 2NaCl \tag{3}$$

ligand adduct of zirconium(III), $[ZrCl_3(P\text{-}n\text{-}Bu_3)_2]_2$, which has an edge-shared bioctahedral structure and a long (3.18 Å) Zr–Zr bond distance.[3] Several other structurally characterized phosphine complexes have since been reported.[4,5]

We are interested in using well-characterized complexes of zirconium(III) halides, in particular Fowles-type pyridine complexes, as starting materials for the preparation of zirconium(III) compounds. As part of these studies, we report herein the straightforward synthesis of pyridine complexes of zirconium(III) chloride, an X-ray structure determination of one derivative, and our initial observations concerning their reactivity, including the apparent oxidation of Zr(III) by an organic nitrile.

Initial attempts to prepare $ZrCl_3(py)_n$ complexes by reducing $ZrCl_4$ in the presence of pyridine (cf. eq 3) led to intractable mixtures. We therefore tried a less direct synthesis that involved the use of preformed zirconium(III) halide complexes. The addition of 4 equiv of pyridine, 4-*tert*-butylpyridine, or 4-(1-butylpentyl)pyridine to a slurry of $[ZrCl_3(P\text{-}n\text{-}Bu_3)_2]_2$ in hexanes gives an immediate reaction and precipitation of a deep red microcrystalline solid. Filtration of the solid and exhaustive washing with hexanes produces material that analyzes as $ZrCl_3(py\text{-}R)_2$. On the basis of this formulation, the yields for eq 4 are nearly quantitative.[6]

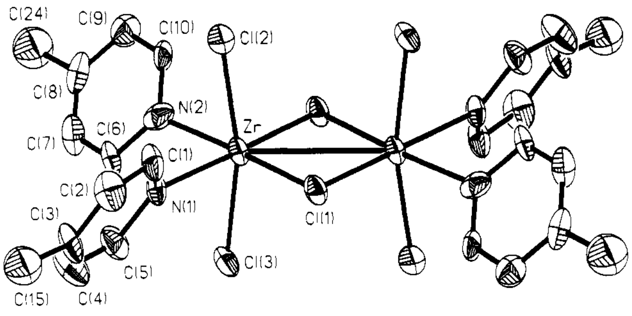


**Figure 1.** Plot of $[ZrCl_3(4\text{-}(1\text{-butylpentyl})pyridine)_2]_2$, showing the atom-numbering scheme (30% probability ellipsoids). The heavily disordered aliphatic chains on the pyridines have been omitted.

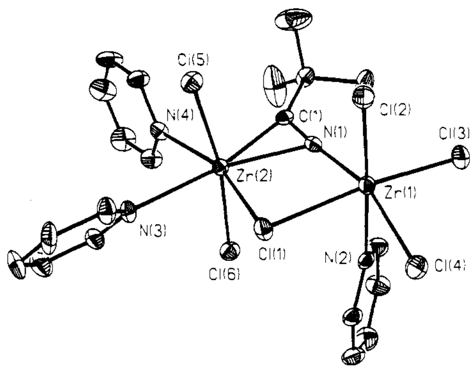


**Figure 2.** Plot of $Zr_2Cl_6(py)_3(t\text{-}BuCN)$, showing the atom-numbering scheme for the core atoms (30% probability ellipsoids).

$$[ZrCl_3(P\text{-}n\text{-}Bu_3)_2]_2 + 4py\text{-}R \xrightarrow[\text{1 h}]{\text{hexanes}} [ZrCl_3(py\text{-}R)]_2 + 4P\text{-}n\text{-}Bu_3 \tag{4}$$

$$R = H,\ 4\text{-}t\text{-}Bu,\ 4\text{-}(1\text{-butylpentyl})$$

The isolation of pyridine adducts via eq 4 prompted us to attempt again a preparation directly from $ZrCl_4$ by reduction with Na/Hg. Despite repeated attempts under various conditions, however, only the 4-(1-butylpentyl)pyridine derivative, the most soluble of the three, could be isolated cleanly (yield: 31%) by this procedure.

The isolated complexes are air sensitive, react with solvents such as thf and $CH_2Cl_2$, and are only sparingly soluble in benzene. $^1H$ NMR spectra recorded for benzene-$d_6$ solutions of the 4-*tert*-butylpyridine and 4-(1-butylpentyl)pyridine derivatives are sharp and unshifted, consistent with a diamagnetic M–M-bonded compound, and reveal only one kind of pyridine. An X-ray structure determination for the 4-(1-butylpentyl)pyridine derivative confirms the dimer formulation (Figure 1).[7] The edge-shared bioctahedral geometry and Zr–Zr distance (3.138 (3) Å) are similar to those of the $[ZrCl_3(PR_3)_2]_2$ complexes.[3,4]

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(1) Ruff, O.; Wallstein, R. *Z. Anorg. Allg. Chem.* **1923,** *128,* 96. Young, R. C. *J. Am. Chem. Soc.* **1931,** *53,* 2148. Larsen, E. M.; Leddy, J. J. *J. Am. Chem. Soc.* **1956,** *78,* 5983. Watt, G. W.; Baker, W. A., Jr. *J. Inorg. Nucl. Chem.* **1961,** *22,* 49. Baker, W. A., Jr.; Janus, A. R. *J. Inorg. Nucl. Chem.* **1964,** *26,* 2087. Swaroop, B.; Flengas, S. N. *Can. J. Chem.* **1964,** *42,* 1495.

(2) Fowles, G. W. A.; Russ, B. J.; Willey, G. R. *J. Chem. Soc., Chem. Commun.* **1967,** 646. Fowles, G. W. A.; Willey, G. R. *J. Chem. Soc. A* **1968,** 1435. Larsen, E. M.; Henzler, T. E. *Inorg. Chem.* **1974,** *13,* 581.

(3) Wengrovius, J. H.; Schrock, R. R.; Day, C. S. *Inorg. Chem.* **1981,** *20,* 1844. Wengrovius, J. H.; Schrock, R. R. *J. Organomet. Chem.* **1981,** *205,* 319.

(4) Cotton, F. A.; Diebold, M. P.; Kibala, P. A. *Inorg. Chem.* **1988,** *27,* 799. Edwards, P. G.; Howard, J. A. K.; Parry, J. S.; Al-Soudani, A.-R. *J. Chem. Soc., Chem. Commun.* **1991,** 1385.

(5) There are some related Cp complexes; see: Chiang, M. Y.; Gambarotta, S.; Bolhuis, F. *Organometallics* **1988,** *7,* 1864 and references therein.

(6) The yields for the pyridine, 4-*tert*-butylpyridine, and 4-(1-butylpentyl)pyridine derivatives were 95, 92, and 83%, respectively. Anal. Calcd for $C_{20}H_{20}Cl_6N_4Zr_2$: C, 33.76; H, 2.83; N, 7.87. Found: C, 33.57; H, 2.79; N, 7.22. Calcd for $C_{36}H_{52}Cl_6N_4Zr_2$: C, 46.20; H, 5.60; N, 5.99. Found: C, 46.29; H, 5.28; N, 5.37. Calcd for $C_{56}H_{92}N_4Cl_6Zr_2$: C, 55.29; H, 7.62; N, 4.60. Found: C, 55.23; H, 7.61; N, 4.23.

(7) Crystal data for $C_{56}H_{92}N_4Cl_6Zr_2$ at −55 (1) °C: dark red plate from benzene/hexanes, 0.55 × 0.45 × 0.12 mm, monoclinic, space group $P2_1/n$, $a$ = 13.869 (8) Å, $b$ = 14.835 (5) Å, $c$ = 16.692 (9) Å, $\beta$ = 111.77 (4)°, $Z$ = 2, $d_{calcd}$ = 1.27 g cm$^{-3}$, and $\mu$ = 6.09 cm$^{-1}$. X-ray diffraction data were collected on a Nicolet R3m/V diffractometer using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å) in the $\theta$–$2\theta$ scan mode. Lorentz and polarization corrections were applied to the data. A total of 3942 reflections were collected in the range 4° < $2\theta$ < 45°; 1890 unique reflections with $I > 3\sigma(I)$ were used in the structure solution. The molecule is situated about an inversion center, and the butylpentyl groups are severely disordered. $R(F)$ = 0.074; $R_w(F)$ = 0.056.

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The intriguing structure (I) proposed by Fowles and co-workers for their Zr(III) acetonitrile complexes[2] prompted us to examine reactions of the $[ZrCl_3(py\text{-}R_2]_2$ compounds with trimethylacetonitrile, which we assumed would give soluble and therefore easily characterizable compounds. Thus, the reaction of 1 equiv of trimethylacetonitrile with $[ZrCl_3(py)_2]_2$ in benzene (3 h) gives an orange solution and precipitate. Workup of the reaction, which includes removal of the volatiles under reduced pressure and a hexanes wash of the residue, produces analytically pure $Zr_2Cl_6(py)_3(t\text{-}BuCN)$ as an orange solid in 92% yield.[8]

An X-ray structure determination for $Zr_2Cl_6(py)_3(t\text{-}BuCN)$ revealed that the nitrile is $\pi$ bound to one Zr center (Zr(2)) and $\sigma$ coordinated via nitrogen to the other (Figure 2).[9] The Zr–Zr distance (3.554 (1) Å) is 0.4 Å longer than in $[ZrCl_3(4\text{-}(1\text{-}butylpentyl)pyridine)_2]_2$, suggesting that the Zr–Zr bond has been cleaved.[10] The Zr(2)–C(1) distance (2.208 (7) Å) is somewhat short compared to Zr–alkyl bond distances (e.g., Zr–C = 2.262 (11) Å in $ZrMe(N(SiMe_3)_2)_3$).[11] Also, the Zr(2)–N(1) and Zr(1)–N(1) distances (2.245 (5) and 2.112 (6) Å) are significantly shorter than the Zr–N(py) bond distances (average 2.391 (11) Å) and Zr(1)–N(1) is nearly as short as the Zr–N distance in $ZrMe(N(SiMe_3)_2)_3$ (2.080 (5) Å),[11] a molecule in which there is undoubtedly some degree of Zr–N multiple bonding.

The coordinated nitrile C–N bond distance (1.255 (9) Å) is lengthened in comparison to the distance in a free nitrile (1.16 Å), and the $Me_3C$–C–N angle (127.4 (7)°) is close to the value expected for $sp^2$ hybridization. This indicates there is significant population of the nitrile $\pi^*$ orbitals. Raman data also support this notion: the C–N stretch has been assigned to a band at 1612 $cm^{-1}$,[12] which is significantly reduced from the value for free nitrile (2237 $cm^{-1}$) and close to the value observed for the C=N bonds in $R_2C{=}NR$ compounds.[13] Thus, the aggregate of structure and spectroscopic properties suggests it is reasonable to count the nitrile as a formal dianionic ligand and to view the reaction to form $Zr_2Cl_6(py)_3(t\text{-}BuCN)$ as an oxidative addition of $t$-BuCN to the Zr–Zr bond in $[ZrCl_3(py)_2]_2$.

In conclusion, we have presented a convenient synthesis of $[ZrCl_3(py\text{-}R)_2]_2$ complexes and the first definitive structural characterization for this type of compound. We have also shown that $t$-BuCN adds to $[ZrCl_3(py)_2]_2$ in an apparent oxidative addition yielding a nitrile ligand coordinated in a $\sigma,\pi$ fashion. Although several examples of $\pi$-bound nitriles to single metal centers are known,[14] a $\sigma,\pi$ coordination mode like that in $Zr_2Cl_6(py)_3(t\text{-}BuCN)$ appears to be rare.[15] Additional reactivity studies are in progress.

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**Supplementary Material Available:** Tables of crystal data, atomic coordinates, and equivalent isotropic displacement parameters for $[ZrCl_3(4\text{-}(1\text{-}butylpentyl)pyridine)_2]_2$ and $Zr_2Cl_6(py)_3(t\text{-}BuCN)$ (4 pages). Ordering information is given on any current masthead page.

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(8) $^1H$ NMR ($CD_2Cl_2$): $\delta$ 9.25 (d, 2, $\alpha$-H, $C_5H_5N$), 9.13 (br, 2, $\alpha$-H, $C_5H_5N$), 8.98 (d, 2, $\alpha$-H, $C_5H_5N$), 7.94 (m, 3, $\gamma$-H, $C_5H_5N$), 7.43 (m, 6, $\beta$-H, $C_5H_5N$), 1.25 (s, 9, $Me_3CCN$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 257.4 ($Me_3CCN$), 152.9 ($\alpha$-C, $C_5H_5N$), 151.7 (br, $\alpha$-C, $C_5H_5N$), 151.4 ($\alpha$-C, $C_5H_5N$), 140.6 (br, $\gamma$-C, $C_5H_5N$), 140.4 ($\gamma$-C, $C_5H_5N$), 140.1 ($\gamma$-C, $C_5H_5N$), 125.5 ($\beta$-C, $C_5H_5N$), 125.2 ($\beta$-C, $C_5H_5N$), 125.1 ($\beta$-C, $C_5H_5N$), 46.5 ($Me_3CCN$), 28.2 ($Me_3CCN$). Anal. Calcd for $C_{20}H_{24}N_4Cl_6Zr_2$: C, 33.57; H, 3.38; N, 7.83. Found: C, 33.39; H, 3.39; N, 7.62.

(9) Crystal data for $C_{20}H_{24}N_4Cl_6Zr_2{\cdot}2CH_2Cl_2$ at −55 (1) °C: orange-red block from cold (−40 °C) $CH_2Cl_2$, 0.70 × 0.45 × 0.40 mm, orthorhombic, space group *Pbca*, $a = 13.980$ (7) Å, $b = 13.743$ (9) Å, $c = 36.843$ (18) Å, $Z = 8$, $d_{calcd} = 1.66$ g $cm^{-3}$, and $\mu = 13.6$ $cm^{-1}$. X-ray diffraction data were collected on a Nicolet R3m/V diffractometer using graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) in the $\omega$ scan mode. Lorentz and polarization corrections and an empirical absorption correction based on $\psi$ scans of 10 reflections having $\chi$ values between 70 and 90° were applied to the data. A total of 4128 reflections were collected in the range $4° < 2\theta < 42°$, and 2823 unique reflections with $I > 3\sigma(I)$ were used in the structure solution. $R(F) = 0.039$; $R_w(F) = 0.035$.

(10) For a different viewpoint on Zr–Zr super long bonds, see: Rohmer, M.-M.; Bénard, M. *Organometallics* **1991**, *10*, 157.

(11) Bradley, D. C.; Chudzynska, H.; Backer-Dirks, J. D. J.; Hursthouse, M. B.; Ibrahim, A. A.; Motevalli, M.; Sullivan, A. C. *Polyhedron* **1990**, *9*, 1423.

(12) The 1612-$cm^{-1}$ band was insensitive to substitution of pyridine by pyridine-$d_5$. The Raman data were obtained via backscattering for a spinning KCl pellet under a $N_2$ atmosphere. See: Czernuszewicz, R. *Appl. Spectrosc.* **1986**, *40*, 571.

(13) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introductions to Infrared and Raman Spectroscopy*, 3rd ed.; Academic: New York, 1990; pp 344–347.

(14) Barrera, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 8178 and references therein.

(15) (a) We know of only one other example for group IV metals, $[Ti(2,6\text{-}diphenylphenoxide)_2(PhCN)]_2$: Rothwell, I. Private communication. For a related late transition metal example, see: Bassi, I. W.; Benedicenti, C.; Calcaterra, M.; Intrito, R.; Rucci, G.; Santini, C. *J. Organomet. Chem.* **1978**, *144*, 255. For a trinuclear example, see: Andrews, M. A.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7260. (b) While this paper was under review, another low-valent example appeared: Alonso, F. J. G.; Sanz, M. G.; Riera, V. *Organometallics* **1992**, *11*, 801.

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## Reversible Cleavage of the Cr–Cr Multiple Bond in $[(TAA)Cr]_2$ (TAA = Tetramethyldibenzotetraaza[14]annulene)

Until the recent discovery that a dichromium moiety with a very short Cr–Cr distance may exist in $[(TAA)Cr]_2$ (TAA = tetramethyldibenzotetraaza[14]annulene) in the absence of any bridging interaction,[1] extremely short Cr–Cr contacts had been found in a particular class of compounds containing bridging three-center chelating ligands[2] and in a few organometallic dimers with bridging carbon donor atoms.[3] The extremely short M–M distances and the magnetic properties of the complexes initially suggested that a strong M–M multiple bond[4] (thought to be quadruple) was the thermodynamic driving force for the dimer formation. However, more recent experimental[5] and theoretical[6] work has established that Cr–Cr quadruple) bonds are para-

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(1) Edema, J. J. H.; Gambarotta, S.; van der Sluis, P.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1989**, *28*, 3782.

(2) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; J. Wiley & Sons: New York, 1982 and references cited therein. (b) Cotton, F. A.; Walton, R. A. Metal-Metal Multiple Bonds in Dinuclear Clusters. *Struct. Bonding (Berlin)* **1985**, *62*, 1. (c) Cotton, F. A.; Feng, X.; Kibala, P. A.; Matusz, M. *J. Am. Chem. Soc.* **1988**, *110*, 2807 and references cited therein. (d) Cotton, F. A.; Koch, S.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2084. (e) Cotton, F. A.; Koch, S. *Inorg. Chem.* **1978**, *17*, 2021. (f) Bino, A.; Cotton, F. A.; Khaim, W. *Inorg. Chem.* **1979**, *18*, 3566. (g) Cotton, F. A.; Koch, S.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2087.

(3) (a) Hursthouse, M. B.; Malik, K. M. A.; Sales, K. D. *J. Chem. Soc., Dalton Trans.* **1978**, 1314. (b) Koschmieder, S. U.; McGillan, B. S.; McDermott, G.; Arnold, J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1990**, 3427. (c) Krausse, J.; Mark, G.; Schoedl, G. *J. Organomet. Chem.* **1970**, *21*, 159. (d) Krausse, J.; Schoedl, G. *J. Organomet. Chem.* **1971**, *27*, 59.

(4) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225.

(5) (a) Larkworthy, L. F.; Tabatabai, J. M. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 427. (b) Sneeden, R. P.; Zeiss, H. H. *J. Organomet. Chem.* **1973**, *47*, 125. (c) Salt, J. E.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 1141. (d) Wilson, L. M.; Cannon, R. D. *Inorg. Chem.* **1988**, *27*, 2382. (e) Cannon, R. D. *Inorg. Chem.* **1981**, *20*, 2341.

(6) Hall, M. B. *Polyhedron* **1987**, *6*, 679 and references cited therein.