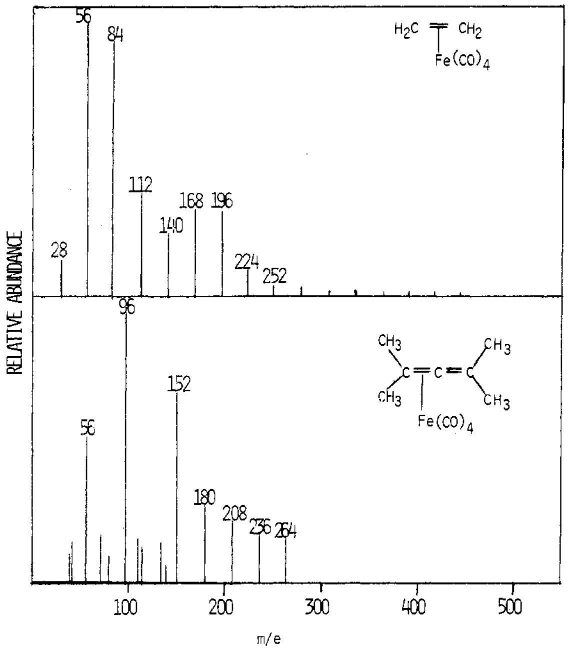

Figure 2. Mass spectra of (tetramethylallene)iron tetracarbonyl and (ethylene)iron tetracarbonyl excited by a 70-eV electron beam.

at high pressure (above 10^{-7} torr)[13,14] but not at the low pressures (ca. 10^{-8} torr) existing in the ionization chamber of our mass spectrometer.[15] We have observed partial sample decomposition for the ethylene complex upon routine vacuum transfer from one vessel to another at ca. 10^{-4} torr. Furthermore, the ethylene complex destroyed our thermal pressure probe on the photoelectron spectrometer, while the TMACO4 sample did not affect it. We would postulate that the metering needle valve on the volatile inlet probe of the photoelectron spectrometer and the gold leak in the mass spectrometer are serving as fractional distillation heads to allow substantial amounts of ethylene and volatile iron carbonyl decomposition products of (ethylene)iron tetracarbonyl into the high-vacuum ionization chambers of the instruments. We further suggest that the broad band (10.01–11.41 eV) in the photoelectron spectrum of (ethylene)iron tetracarbonyl which has been assigned[1,2] to an unperturbed ethylene π orbital really refers to a mixture of complexed and free ethylene, such that the true vertical ionization potential for the complex is not resolved.

Acknowledgment. The authors thank D. H. Gibson of the University of Louisville for a sample of (tetramethylallene)iron tetracarbonyl and for helpful comments about this work. They also thank P. Martino for assistance in sample handling. The support of the Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. TMACO$_4$, 12264-26-5; TMA, 1000-87-9; (CH_2=CH_2)Fe(CO)$_4$, 32799-25-0.

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(11) A referee has suggested that since the two d orbital band components for Fe(CO)$_5$ have equal intensity and are split by ca. 1 eV our assignment for TMACO4 be revised to 7.84 and 8.50 eV for iron orbitals and 8.24 and 9.28 eV for the ligand orbitals. There is a problem with this assignment. It implies that Fe(CO)$_4$ perturbs the two π orbitals of TMA in opposite directions. Such behavior has not been observed for any of the 11 Fe(CO)$_3$ complexes of dienes studied in these laboratories;[10] the latter complexes would seem to be better models for TMACO4 than is Fe(CO)$_5$. However, as suggested by the referee, a comparison of He I and He II spectra would be useful for deciding between the two assignments. In any case the π orbital is *not* unperturbed by Fe(CO)$_4$.
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Contribution from the Central Research and Development
Department, E. I. du Pont de Nemours and Company,
Experimental Station, Wilmington, Delaware 19898

Bridging Alkylimido Complexes of the Group 4B Transition Metals

William A. Nugent* and R. L. Harlow

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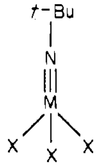
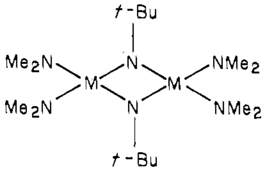
Recently we reported the preparation of group 5B alkylimido complexes of niobium and tantalum[1] and of vanadium.[2] Monomeric complexes Ia–c contain a nearly linear M–N–C arrangement indicating that the formal double bond from metal to nitrogen in fact has considerable triple bond character. In contrast, the known organoimido derivatives of titanium have either dimeric or polymeric structures.[3-5] For instance, compound IIa was prepared by Bradley[3] and a dimeric structure was assigned from solution molecular weight measurements. We have now prepared the zirconium[6] and hafnium analogues IIb and c and have found that these species are imido nitrogen-bridged dimers.

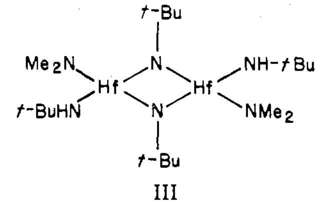


Ia, M = V, X = OSiMe$_3$
b, M = Nb, X = NMe$_2$
c, M = Ta, X = NMe$_2$



IIa, M = Ti
b, M = Zr
c, M = Hf

Refluxing a hexane solution of tetrakis(dimethylamido)hafnium containing 1 equiv of *tert*-butylamine causes the initially colorless solution to become yellow. Removal of the solvent at reduced pressure gave a yellow residue which contained no IIc by NMR.[7] However, heating this material at 150 °C in vacuo afforded a yellow sublimate which was largely IIc apparently contaminated with compound III.[8] The product was purified by recrystallization. Zirconium derivative IIb was prepared in an analogous manner. However, the major impurity in the sublimate in this case appears to be Zr(NMe$_2$)$_4$.



III

Table I. NMR Chemical Shift Data[a] for d° Four-Coordinate *tert*-Butylimido Complexes

complex	color	J (^{1}H), ppm t-Bu	J (^{1}H), ppm NMe	J (^{13}C), ppm primary t-Bu	J (^{13}C), ppm tertiary t-Bu	J (^{13}C), ppm NMe
Ia	yellow	1.22	–[b]	30.74	–[c]	–[d]
Ib	yellow	1.39	3.16	33.47	68.63	46.92
Ic	white	1.43	3.20	34.57	66.68	46.08
IIa	red	1.19	3.42	34.57	69.67	45.88
IIb	yellow-green	1.25	3.16	35.74	63.17	42.83
IIc	pale blue	1.24	3.23	36.59	61.42	42.37

[a] In 0.5 M toluene-d_8 solution vs. 1% internal Me_4Si except compound IIa which was 0.1 M. [b] SiMe resonance observed at δ 0.25. [c] Not observed. [d] SiMe resonance observed 2.34 ppm downfield from Me_4Si.

Table II. Selected Bond Distances (Å) with Estimated Standard Deviations

Zr· · ·Zr′	3.092 (1)	N(2)–C(5)	1.443 (3)
Zr–N(1)	2.071 (1)	N(2)–C(6)	1.444 (3)
Zr–N(1)′	2.060 (1)	N(3)–C(7)	1.445 (2)
Zr–N(2)	2.057 (1)	N(3)–C(8)	1.443 (3)
Zr–N(3)	2.062 (1)	C(1)–C(2)	1.517 (3)
N(1)–C(1)	1.475 (2)	C(1)–C(3)	1.524 (3)
		C(1)–C(4)	1.518 (3)

^{1}H and ^{13}C chemical shift data for compounds II as well as those for compounds I are collected in Table I. Comparison of the ^{13}C *tert*-butyl resonances for a given group 4 complex with those of the corresponding group 5 derivative is noteworthy: as we proceed from group 4 to group 5, the methyl carbon resonance shifts upfield, but the quarternary carbon resonance shifts downfield. These shifts are consistent with greater electron density on nitrogen in the group 4 derivatives. In accord with this observation, the linear M–N–C arrangement in compounds I indicates effective nitrogen p to metal d electron donation. Similarly, the data for both compounds I and compounds II indicate increasing electron density on nitrogen with increasing atomic number. We attribute this to increasing orbital mismatch between nitrogen and metal as we proceed from first- to second- to third-row derivatives.

Several factors militate against a monomeric structure in the group 4 complexes. A multiply bonded *tert*-butylimido structure analogous to compounds I would result in severe coordinative unsaturation (three-coordination) in compounds II. Moreover the long metal–nitrogen bond anticipated for such a hypothetical group 4 complex would result in greater separation of charge (M^+–N^-) than in the group 5 derivatives. Chemical evidence is also consistent: Reaction of compounds II with *tert*-butyl alcohol results in cleavage of all metal–nitrogen bonds to afford the corresponding tetrakis(*tert*-butoxide). In contrast, alcoholysis of the multiply bonded ethylimido ligand in $(Et_2N)_3Ta(NEt)$ proceeds only under more vigorous conditions.[9]

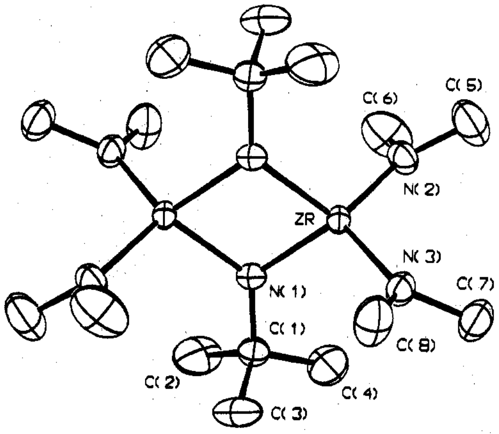


Figure 1. Structure of $[(\mu\text{-N-}t\text{-Bu})Zr(NMe_2)_2]_2$ showing the numbering scheme.

Table III. Selected Bond Angles (deg) with Estimated Standard Deviations

N(1)-Zr-N(1)′	83.10 (5)	Zr-N(2)-C(5)	119.1 (2)
N(1)-Zr-N(2)	116.27 (6)	Zr-N(2)-C(6)	129.7 (2)
N(1)-Zr-N(3)	112.87 (5)	C(5)-N(2)-C(6)	110.7 (2)
N(1)′-Zr-N(2)	112.87 (6)	Zr-N(3)-C(7)	123.5 (1)
N(1)′-Zr-N(3)	113.80 (5)	Zr-N(3)-C(8)	125.7 (1)
N(2)-Zr-N(3)	114.28 (6)	C(7)-N(3)-C(8)	110.6 (2)
Zr-N(1)-Zr′	96.90 (5)	N(1)-C(1)-C(2)	109.2 (2)
Zr-N(1)-C(1)	126.8 (1)	N(1)-C(1)-C(3)	110.1 (2)
Zr′-N(1)-C(1)	131.3 (1)	N(1)-C(1)-C(4)	109.8 (2)

The dimeric structure of IIb is confirmed by an X-ray crystal structure as shown in Figure 1. Selected bond lengths and angles are shown in Tables II and III. Each zirconium atom exhibits roughly tetrahedral coordination. The dimethylamido ligands are nearly planar. The two zirconium atoms together with the two imido nitrogens form a plane from which C(1) deviates by 0.458 (2) Å. The bonds from bridging nitrogen to each zirconium atom are equal within experimental error. Symmetrically bridged nitrogens have also been observed in all other bridging imido derivatives which have been structurally characterized to date.[10] In contrast, a number of unsymmetrically bridged nitrido complexes are known.[11] The zirconium to imido nitrogen bonds in IIb (average 2.066 (1) Å) are considerably longer than those in a (formally) double-bonded niobium derivative (1.752 (6) Å).[12] Moreover the Zr to imido nitrogen bond length of IIb is not significantly different from the length of the Zr to amido nitrogen bonds (average 2.060 (1) Å). Thus it is anticipated that the chemistry of IIb will be essentially that of a tetrakis(amido) derivative.

Experimental Section

Materials. Hexane, toluene, and *tert*-butylamine were sparged with nitrogen and dried over 5A molecular sieves prior to use. All reactions and subsequent manipulations were carried out under dry nitrogen.

Preparation of Complexes. Bis[μ-(N-*tert*-butylimido)]-bis(dimethylamido)dihafnium (IIc) was prepared by refluxing 3.55 g (10 mmol) of $Hf(NMe_2)_4$ with 0.73 g (10 mmol) *tert*-butylamine in 25 mL of hexane for 3 h. After removal of solvent the waxy yellow residue was sublimed to afford the desired product contaminated with III. Pure IIc was obtained by twice dissolving the sublimate in 5 mL of hexane and cooling the mixture to −35 °C. Yields varied but typically were ca. 20%.

Bis[μ-(N-*tert*-butylimido)]-bis(dimethylamido)dizirconium (IIb) was prepared analogously. The side product $Zr(NMe_2)_4$ in the sublimate was not diminished by increasing the amount of *tert*-butylamine used in the synthesis. Purification was facilitated by manually separating white crystals of $Zr(NMe_2)_4$ from the green crystals of IIb after the first recrystallization. X-ray quality crystals of IIb were grown by slowly cooling a dilute toluene solution to −40 °C. The crystal selected for X-ray study was a parallelpiped measuring 0.20 × 0.22 × 0.30 mm. It was mounted in a quartz capillary with the c axis of the crystal nearly parallel to the length of the capillary.

Structural Details. Data were collected on a Syntex $P3$ diffractometer with the crystal cooled to −20 °C (graphite monochromator; Mo Kα radiation; λ 0.710 69 Å). Axial photographs and systematic absences were consistent with the monoclinic space group $P2_1/n$. The unit-cell dimensions were refined from the Bragg angles (as determined by the Syntex centering routine) of 50 reflections in the range $24° < 2\theta < 26°$: $a = 9.570$ (1) Å, $b = 16.314$ (2) Å, $c = 8.764$ (1) Å, $\beta = 114.84$ (1)°. The cell volume, 1241.7 Å^3, yields a calculated density of 1.340 g cm^{-3} for $Z = 2$.

Intensity data for 2852 reflections were collected by using the ω-scan technique ($4° < 2\theta < 55°$; scan width of 1.0°; variable scan rate of 2.0–5.0° min^{-1}; background measurements at both ends of the scan; total background time equal to scan time). The intensities of four standard reflections were monitored after every 100 reflections; the average intensity decreased by 15% and a decay correction was thus applied. The intensity of the (−2,3,5) reflection was measured in 10° increments about the diffraction vector; as a result, empirical absorption correction factors ranging from 1.00 to 1.12 were applied (the linear absorption coefficient is 8.3 cm^{-1}).

The solution and refinement of the structure were carried out on a PDP-11 computer using local modifications of the programs supplied by the Enraf-Nonius Corp.[13] The atomic scattering factors were taken from the tabulations of Cromer and Waber;[14a] anomalous dispersion corrections were by Cromer.[14b] In the least-squares refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weights, w, assigned as $1/\sigma^2(F_o)$. The standard deviations of the observed structure factors, $\sigma(F_o)$, were based on counting statistics and an "ignorance factor", p, of 0.02.[15]

The structure was solved by direct methods. The positions of the hydrogen atoms were determined by Fourier difference techniques. Full-matrix least-squares refinement of all positional and thermal parameters (anisotropic for Zr, N, and C; isotropic for H) with the 2459 reflections with $I > 2\sigma(I)$ converged at

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.023$$

$$R = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.025$$

The two largest peaks in the final difference Fourier had magnitudes of approximately 0.3 e $\mathrm{Å}^{-3}$ and were located near Zr and N(1).[16]

Registry No. Ia, 70024-35-0; Ib, 69039-12-9; Ic, 69039-11-8; IIa, 70024-36-1; IIb, 70024-37-2; IIc, 70024-38-3; $Zr(NMe_2)_4$, 19756-04-8; $Hf(NMe_2)_4$, 19782-68-4.

Supplementary Material Available: Tables of final positional parameters (as fractional coordinates), thermal parameters, and structure factor amplitudes (observed and calculated) (22 pages). Ordering information is given on any current masthead page.

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(14) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974: (a) Table 2.2B; (b) Table 2.3.1.
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(16) We have recently determined the structure of IIa and have found it to be isostructural with IIb with average Ti–N(imido) = 1.923 (2) Å and Ti–N(amido) = 1.913 (2) Å. Details will be published elsewhere.

Contribution from the Department of Chemistry,
Illinois Institute of Technology, Chicago, Illinois 60616

Some Complexes of Cobalt(III) with 3,6-Diaza-1,9-nonanediamine, an Unsymmetrical Flexible Tetraamine Ligand

George R. Brubaker,* Frank H. Jarke,[1] and Inara M. Brubaker

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As a part of our continuing investigation of the stereochemistry of complexes with flexible tetradentate ligands, we have synthesized and characterized some complexes with the unsymmetrical tetraamine ligand 3,6-diaza-1,9-nonanediamine, 2,2,3-tet. The ligand 2,2,3-tet is a structural isomer of 3,7-diaza-1,9-nonanediamine, 2,3,2-tet, complexes of which have been extensively studied.[2] Our interest in unsymmetrical ligands arises from our expectation that the differing terminal chain lengths will give rise to geometrical specificity in complexes with these ligands. Thus, while it is well established that the symmetrical ligand 2,3,2-tet readily forms trans and unsymmetrical-cis complexes, it is not possible to control which of the terminal donor atoms moves in the course of well-known trans–cis isomerization reactions.[3] We expect that internal strain will favor the displacement of one of the terminal donors; i.e., either the "short" or the "long" terminal ring should be preferentially displaced from the plane of the tetraamine ligand in the parent trans complex. We report herein the synthesis of several complexes, details of the electronic spectra, details of a ^{1}H NMR study of several examples, and the results of a strain-energy minimization calculation.

Experimental Section

Synthetic Procedures. Preparation of 3,6-Diaza-1,9-nonanediamine, 2,2,3-tet. A 1-mol sample of acrylonitrile was refluxed overnight with 1.5 mol (excess) of *N*-(2-aminoethyl)ethylenediamine in 250 mL of benzene. After evaporation of the benzene, the product was hydrogenated with Raney nickel as the catalyst in ammoniacal absolute ethanol until the precise amount of hydrogen to effect reduction had been taken up. The mixture was then filtered to remove the Raney nickel and then the product was vacuum distilled at 140–145 °C (9 mm).

Preparation of *trans*-Dichloro(3,6-diaza-1,9-nonanediamine)cobalt(III) Chloride, *trans*-[Co(2,2,3-tet)Cl_2]Cl. 3,6-Diaza-1,9-nonanediamine (1.5 g, 0.1 mol) was added to a solution of $CoCl_2\cdot 6H_2O$ (2.4 g, 0.1 mol) in 200 mL of water. A stream of air previously passed through KOH solution to remove CO_2 was bubbled through the solution for 16 h. To the red solution was added 25 mL of concentrated HCl, and it was evaporated to near dryness on a steam bath. After the solution was cooled, the crude green product was removed by filtration, washed with ethanol, recrystallized from hot water, and dried at 110 °C for 24 h. Anal. Calcd for $CoC_7H_{20}N_4Cl_3$: C, 25.81; H, 6.20; N, 17.21. Found: C, 25.73; H, 6.48; N, 17.16.

Preparation of *uns-cis*-(Valinato)(3,6-diaza-1,9-nonanediamine)cobalt(III) Perchlorate, *uns-cis*-[Co(2,2,3-tet)val]$(ClO_4)_2$. The pH of a solution containing 1.17 g (4 mmol) of *trans*-[Co(2,2,3-tet)Cl_2]Cl and 0.46 g (4 mmol) of L-valine in 10 mL of water was adjusted to 5.5. The solution was heated at 60 °C with stirring for 1 h. The pH was then adjusted to 8.5 and the stirring continued for 2 h. The complex crystallized upon addition of $LiClO_4$. The solution was filtered and the crystals were washed with ether and air-dried. Anal. Calcd for $CoC_{12}H_{30}N_5Cl_2O_{10}$: C, 26.96; H, 5.66; N, 13.11. Found: C, 26.61; H, 5.74; N, 12.79.

Preparation of *trans*-Bis(acetato)(3,6-diaza-1,9-nonanediamine)cobalt(III) Perchlorate, *trans*-[Co(2,2,3-tet)$(OAc)_2$]ClO_4. A solution containing 1.3 g (4 mmol) of *trans*-[Co(2,2,3-tet)Cl_2]Cl and 5.2 g (8 mmol) of sodium acetate was warmed at 60 °C for 2 h after which excess potassium perchlorate was added and the solution cooled. The large red crystals were removed by filtration, washed with acetone, and air-dried. Anal. Calcd for $CoC_{11}H_{26}N_7ClO_8$: C, 30.23; H, 6.00; N, 12.83. Found: C, 29.98; H, 5.87; N, 12.58.

Preparation of *trans*-Bis(sarcosine)(3,6-diaza-1,9-nonanediamine)cobalt(III) Perchlorate, *trans*-[Co(2,2,3-tet)$(sarc)_2$]$(ClO_4)_3$. To a solution containing 1 g of *trans*-[Co(2,2,3-tet)Cl_2]Cl and 1.5 g of sarcosine in 15 mL of water was added 5 N NaOH to adjust the pH to 5.5. The solution was heated at 40 °C for 16 h. On addition of 1 g of potassium perchlorate and cooling of the solution, the red crystals formed and were removed by filtration. Anal. Calcd for $CoC_{13}H_{34}N_6Cl_3O_{16}$: C, 22.46; H, 4.93; N, 12.10. Found: C, 22.57; H, 4.93; N, 11.91.

Preparation of *uns-cis*-(Oxalato)(3,6-diaza-1,9-nonanediamine)cobalt(III) Iodide, *uns-cis*-[Co(2,2,3-tet)ox]I. To a constantly stirred solution containing 1.30 g (4 mmol) of *trans*-[Co(2,2,3-tet)Cl_2]Cl was added 0.75 g (4 mmol) of potassium oxalate hydrate in 14 mL of water. The solution was warmed at 60 °C for 3 h and filtered and the filtrate evaporated at 60 °C until crystals began to form. The solution was placed in the refrigerator for 3 h. The needlelike crystals

0020-1669/79/1318-2032$01.00/0