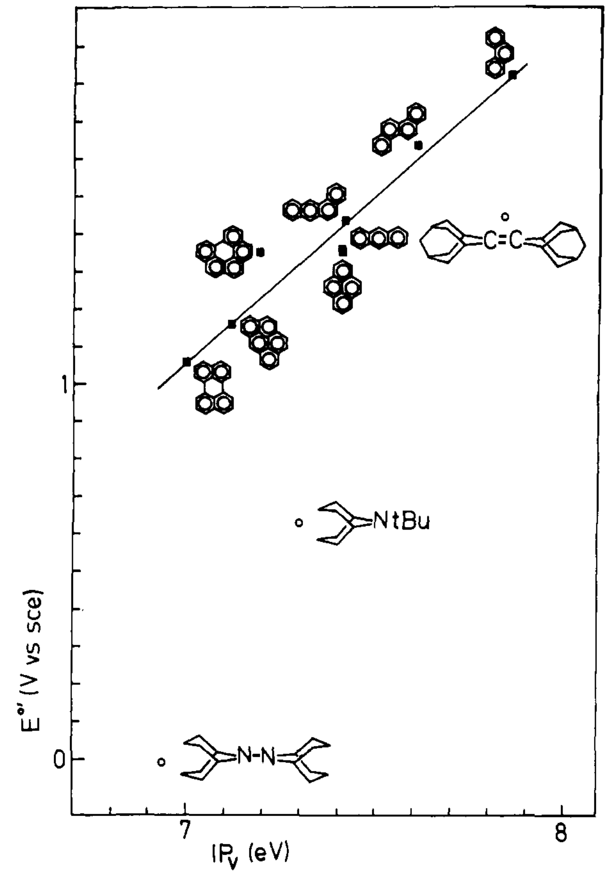


Figure 1. Plot of $E^{\circ\prime}$ (V vs. SCE in CH_3CN) vs. IP_v (eV) for fused aromatic hydrocarbons, compared with **1**, **3**, and **4**.

giving $E^{\circ\prime} = -5.21 + 0.89_5\,(IP_v)$.[11] There is a large lowering of IP_v for substitution of methyl for hydrogen of olefins (ethylene, 10.51 eV; tetramethylethylene, 8.42 eV[12]) and the additional lowering observed when alkyl groups are lengthened makes the observed IP_v for **4** of 7.84 eV not at all surprising.[13] $E^{\circ\prime}$ for **4**-$\mathbf{5}^{+\cdot}$ is approximately −0.36 V (8.3 kcal/mol below the aromatic hydrocarbon line), as shown graphically in Figure 1. The far smaller π system of $\mathbf{4}^{+\cdot}$ and its aliphatic substituents are expected to make solvent stabilization of $\mathbf{4}^{+\cdot}$ substantially different from that for the fused aromatic hydrocarbons used to determine the line shown. It is thermodynamically significantly easier to remove lone-pair electrons from **3** ($E^{\circ\prime}$ = −0.01 V,[3] vertical deviation from the hydrocarbon line −1.01 V) and **1** ($E^{\circ\prime}$ = +0.63 V,[1] vertical deviation −0.69 V), much more so than IP_v differences would suggest. Although solvation differences among **1**, **3**, and **4** cannot be ignored, we suggest that the most significant factor is the large rehybridization at nitrogen which occurs upon electron removal from **3**[14] and **1**; comparable rehybridization will not occur for **4**, which is already sp^2 hybridized at the vinyl carbons.

A particularly significant difference between the oxidation behavior of **3** and **4** involves removal of a second electron. The second oxidation wave in the CV of **3** is electrochemically reversible, and $E^{\circ\prime}_2 - E^{\circ\prime}_1$ is 1.19 V, the largest value yet reported for a compound showing two reversible electron transfers.[3] In contrast, **4** in acetonitrile shows a completely irreversible second oxidation wave peaking at +1.96 V (scan rate 100 mV/s), only 0.51 V positive of $E^{\circ\prime}_1$. Although the $\mathbf{3}^{+\cdot}/\mathbf{3}^{2+}$ and $\mathbf{4}^{+\cdot}/\mathbf{4}^{2+}$ couples have the same charge and similar alkyl group structures (we presume the remote methylenes of **4** are relatively unimportant), they are not isoelectronic. The third, antibonding π electron of $\mathbf{3}^{+\cdot}$ is reversibly removable, but the single π electron of $\mathbf{4}^{+\cdot}$ should be strongly bonding. Because of the small difference in potentials at which a second electron is removed from **4**, we suggest that the carbon-centered two-atom π dication which would be the hydrocarbon analogue of $\mathbf{3}^{2+}$ may not be formed and that the second electron removed may well be a σ electron which would be expected to cause rapid deprotonation and hence be irreversible, by analogy to the behavior of adamantane upon electrochemical oxidation.[15,16]

References and Notes

(1) Kelly, R. P.; Lindsay-Smith, J. R. *J. Chem. Soc., Chem. Commun.* **1978**, 320.
(2) Nelsen, S. F.; Kessel, C. R. *J. Chem. Soc., Chem. Commun.* **1977, 490.**
(3) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1977,** *99,* 2392.
(4) Danen, W. C.; Rickard, R. C. *J. Am. Chem. Soc.* **1972,** *94,* 3254; Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1973,** *95,* 6400.
(5) Segal, B. G.; Kaplan, M.; Fraenkel, G. K. *J. Chem. Phys.* **1965,** *43,* 4191.
(6) Carter, M. K.; Vincow, V. *J. Chem. Phys.* **1967,** *47,* 302.
(7) Stone, A. J. *Mol. Phys.* **1963,** *6,* 509; **1964,** *7,* 311.
(8) McConnell, H. M.; Robertson, R. P. *J. Phys. Chem.* **1957,** *61,* 1018.
(9) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972,** *37,* 316.
(10) Parker, V. D. *J. Am. Chem. Soc.* **1976,** *98,* 98.
(11) For a comparison of $E^{\circ\prime}$ vs. IP_v correlations for trisubstituted nitrogen compounds and aromatic hydrocarbons, see Nelsen, S. F. *Isr. J. Chem.*, in press.
(12) Fuss, W.; Bock, H. *J. Chem. Phys.* **1974,** *61,* 1613.
(13) Mollere, P. D.; Houk, K. N.; Bomse, D. S.; Morton, T. H. *J. Am. Chem. Soc.* **1976,** *98,* 4732.
(14) Nelsen, S. F.; Hollinsed, W. C.; Kessel, C. R.; Calabrese, J. C. *J. Am. Chem. Soc.* **1978,** *100,* 7876.
(15) Miller, L. L.; Koch, V. R.; Koenig, T.; Tettle, M. *J. Am. Chem. Soc.* **1973,** *95,* 5075. Koch, V. R.; Miller, L. L. *ibid.* **1973,** *95,* 8631.
(16) We thank the National Science Foundation for partial financial support of this research under Grants 74-19688 and 77-24627, as well as the major instrument program, and the Graduate School of the University of Wisconsin for a Fellowship to C.R.K. Dr. E. L. Clennan kindly provided the sample of **4** employed.

Stephen F. Nelsen,* Carl R. Kessel
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received January 18, 1979

Tetradecaisopropoxydihydridotetratungsten(IV). Oxidative Addition of PrO–H across a Tungsten-to-Tungsten Triple Bond

Sir:

Bimetallic compounds containing metal-to-metal multiple bonds[1] will occupy an important position in the development of transition metal cluster chemistry.[2] They are the smallest examples of unsaturated cluster compounds and should provide building blocks for the synthesis of new polynuclear cluster compounds. Furthermore their reactions should complement those well documented in mononuclear transition metal chemistry.[3] We now report the preparation and characterization of a novel tetranuclear tungsten compound which illustrates these considerations.

Hydrocarbon solutions of $W_2(NMe_2)_6(W{\equiv}W)$[4] react rapidly with 2-propanol at room temperature with the liberation of amine. Upon removal of the solvent a black solid of empirical formula $W(OPr^i)_3$ based on elemental analysis[5] was obtained. The black substance gave very complex NMR spectra and was thermally unstable yielding propylene, 2-propanol, and traces of water as volatiles when heated above 80 °C in vacuo. These observations contrast with the reaction between $Mo_2(NMe_2)_6$ and 2-propanol which yields the thermally stable and well-characterized compound $Mo_2(OPr^i)_6(Mo{\equiv}Mo)$.[6] Additional study of the reaction between $W_2(NMe_2)_6$ and 2-propanol in a sealed system showed that along with dimethylamine a gas noncondensable in liquid N_2 was formed. The latter was identified as molecular hydrogen by mass spectroscopy. The solids obtained from the reaction between $W_2(NMe_2)_6$ and 2-propanol are extremely soluble

0002-7863/79/1501-2504$01.00/0

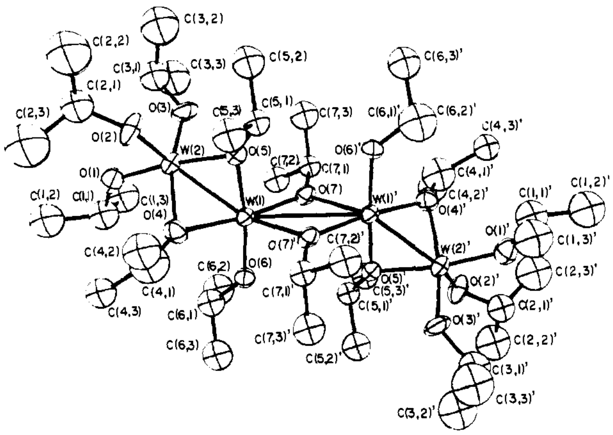


Figure 1. A view of the entire $W_4(OPr^i)_{14}(\mu\text{-}H)_2$ molecule, omitting the μ-H atoms.

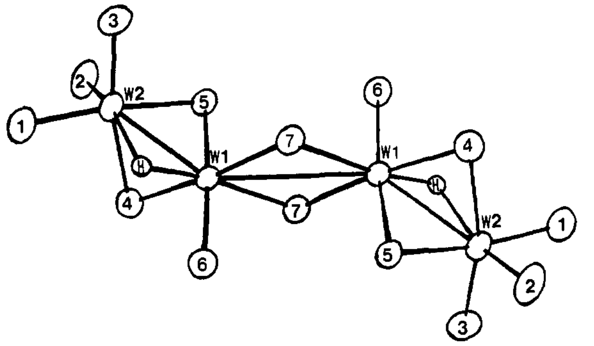


Figure 2. A view of the $W_4O_{14}H_2$ skeleton, showing the bridging hydrogen atoms.

Table I. Some Bond Lengths and Angles in $W_4(OPr^i)_{14}H_2$[a]

distances, Å		angles, deg	
W(1)-W(1)'	3.407 (1)	O(4)-W(1)-O(5)	78.2 (3)
W(1)-W(2)	2.446 (1)	O(4)-W(1)-O(6)	91.7 (3)
W(1)-O(4)	2.101 (7)	O(4)-W(1)-O(7)	173.4 (3)
W(1)-O(5)	2.005 (7)	O(4)-W(1)-O(7)'	107.6 (3)
W(1)-O(6)	2.897 (6)	O(5)-W(1)-O(7)	95.2 (3)
W(1)-O(7)	2.038 (6)	O(5)-W(1)-O(7)'	86.6 (3)
W(1)-O(7)'	2.187 (6)	O(5)-W(1)-O(6)	168.6 (3)
W(2)-O(1)	1.904 (8)	W(1)-O(4)-W(2)	70.9 (2)
W(2)-O(2)	1.959 (7)	W(1)-O(5)-W(2)	73.1 (2)
W(2)-O(3)	1.892 (7)	O(1)-W(2)-O(2)	91.9 (3)
W(2)-O(4)	2.116 (6)	O(1)-W(2)-O(3)	94.3 (3)
W(2)-O(5)	2.100 (7)	O(2)-W(2)-O(3)	101.7 (3)
		O(1)-W(2)-O(4)	94.5 (3)
		O(1)-W(2)-O(5)	169.9 (3)
		O(2)-W(2)-O(4)	90.5 (3)
		O(2)-W(2)-O(5)	85.2 (3)
		O(3)-W(2)-O(4)	164.6 (3)
		O(3)-W(2)-O(5)	95.8 (3)

[a] We give here the final values after refinement with the μ-H atoms included. These differ by only about <0.004 Å or <0.01° from those obtained without the μ-H atoms.

in hexane and give upon careful crystallization the title compound $W_4(OPr^i)_{14}H_2$ in ~50% yield based on tungsten.

The presence of hydrogen atoms in bridging positions was deduced in the following way.

(1) An X-ray crystallographic study[7] initially showed the structure in Figure 1, with the bond distances and angles in Table I. The molecule resides on a crystallographic inversion center (between W(1) and W(1)'). The outer tungsten atoms, W(2) and W(2)', are coordinated to three terminal and two bridging OPr^i ligands while the inner tungsten atoms, W() and W(1)', are coordinated to one terminal and four bridging OPr^i ligands. Each tungsten atom is thus coordinated to five oxygen atoms and the WO_5 polyhedra are distorted square pyramids.

(2) According to these results the compound would have to be either a mixed valence compound, $W_4(OPr^i)_{14}$, or an alcoholate, $W_4(OPr^i)_{12}(Pr^iOH)_2$. The mixed valence formulation would have difficulty accounting for the diamagnetism (as shown by NMR) and is more directly discredited by the observation that reaction of $W_2(NMe_2)_6$ with 2-propanol containing Pr^iOT gave a product containing tritium.[8]

(3) However, the presence of Pr^iOH was rendered very doubtful by the absence of any IR or NMR evidence for a hydroxyl group and by the fact that the compound does not react with pyridine to form $W_2(OPr^i)_6(py)_2$, even though the latter compound has been shown to exist and has been fully characterized[9] as a species containing a triple bond ($W{\equiv}W$ = 2.332 (1) Å).

(4) These results required us to search for some other formulation and we were reminded of the $[Mo_2X_8H]^{3-}$ ions[10] which have recently been shown directly by X-ray crystallography[11] to contain μ-H atoms. The apparent absence of one bridging ligand between the two tungsten atoms in each half of the tetratungsten structure was highly reminiscent of the apparent[10a,b] absence of a third bridging ligand in the $[Mo_2X_8H]^{3-}$ species, later shown to be present as a hydrogen atom.[10c,11] To test the correctness of the formula $W_4(OPr^i)_{14}(\mu\text{-}H)_2$, the following two experiments were done.

(5) The ^1H NMR spectrum at 220 MHz in toluene-d_8 and benzene-d_6 at 25 °C was found to contain, in addition to the expected Pr^iO resonances (1.34 (doublet) and 5.27 ppm (septet), each with $J_{HH} \approx 6.3$ Hz), a singlet at 7.96 ppm (all positions downfield from Me_4Si). The singlet had satellites due to coupling to ^{183}W ($I = \frac{1}{2}$; 14.4% of natural abundance) with $J_{WH} = 95$ Hz. Since a cryoscopic molecular weight measurement had shown that the tetranuclear structure is largely or totally maintained in solution, we are forced to attribute the simplicity of the spectrum to some process that scrambles the OPr^i groups. Since only one pair of satellites is observed on the 7.96-ppm signal, this same process (or some other one) must make the tungsten atoms equivalent so that we see only one $^{183}W\text{-}^1H$ coupling constant. It should be remembered that we see only those molecules that contain one ^{183}W.

(6) We now returned to the X-ray data, encouraged by the fact that in the $[Mo_2X_8H]^{3-}$ ions[11] and in numerous other species with $M(\mu\text{-}H)M$ units the μ-H atoms have been detected and refined. We have found that there is evidence for a μ-H atom between W(1) and W(2) and that it can be refined successfully as such, to give W(1)-H = 1.61 (8) Å, W(2)-H = 1.89 (8) Å, W-H-W = 88 (4)° with the isotropic temperature factor for μ-H equal to 1 ± 2 Å^2.

We therefore conclude that each tungsten atom is six coordinate as shown in Figure 2. All qualitative features of the structure are now understandable. The W-O bonds trans to μ-H are considerably longer than those trans to μ-OPr^i, which exactly parallels the situation in the $[Mo_2Cl_8H]^{3-}$ ion.[11] The μ-H is closer to W(1) so as to minimize the imbalance in electron density distribution that the difference in formal oxidation numbers in a symmetrical structure W(1) = $+3\frac{1}{2}$ and W(2) = $+4\frac{1}{2}$) would tend to create.

Formation of the title compound in the reaction between $W_2(NMe_2)_6$ and Pr^iOH may be attributed to the following reaction steps: (i) alcoholysis, $W\text{-}NMe_2 + Pr^iOH \rightarrow W\text{-}OPr^i + HNMe_2$; (ii) oxidative addition, $W_2(OPr^i)_6 + Pr^iOH \rightarrow W_2(OPr^i)_7(\mu\text{-}H)$; (iii) association by Pr^iO bridge formation. The W(1)-W(1)' distance implies no metal-metal bonding, whereas the W(1)-W(2) distance, 2.446 (1) Å, is quite consistent with the presence of a $W{=}W$ bond.[12] Our studies on these and related compounds are continuing.[13]

Supplementary Material Available: Table of positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) For recent reviews of compounds containing metal-to-metal multiple bonds, see F. A. Cotton, *Acc. Chem. Res.*, **11,** 225 (1978); M. H. Chisholm and F. A. Cotton, *ibid.*, **11,** 356 (1978); M. H. Chisholm, *Transition Met. Chem.*, (*Weinheim, Ger.*) **3,** 321 (1978).

(2) Potential catalytic implications of cluster chemistry have recently been discussed. See E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84,** 959 (1974); E. L. Muetterties, *Science*, **196,** 839 (1977); R. Ugo, *Catal. Rev.*, **11,** 225 (1975).

(3) For a classification of organometallic reactions, see C. A. Tolman *Chem. Soc. Rev.*, **1,** 337 (1972).

(4) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98,** 4477 (1976).

(5) Anal. Calcd: C, 29.93; H, 5.86. Found: C, 30.2; H, 5.96.

(6) M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, *Inorg. Chem.*, **16,** 1801 (1977).

(7) Cell constants: a = 12.645 (4), b = 13.157 (4), c = 9.788 (3) Å; α = 102.43 (2), β = 67.80 (2), γ = 101.05 (2)°; V = 1461.5 (7) Å^3. The structure was solved in the centrosymmetric space group $P1$. A total of 3782 unique data having $0° < 2\theta$ Mo K$\alpha < 45.0°$ were measured, of which those 2949 having $I > 3\sigma(I)$ were used in subsequent refinement. All atoms were refined to convergence utilizing anisotropic thermal parameters for the tungsten and oxygen atoms and isotropic thermal parameters for the carbon atoms. The final cycle of least-squares refinement, including the μ-H atoms, gave R_1 = 0.037 and R_2 = 0.052. A table of atomic positional and thermal parameters is available as supplementary material. See the paragraph at the end of the paper.

(8) We thank Professor Charles Gilvarg of the Department of Biochemistry Princeton University for his assistance and guidance in these experiments.

(9) This compound is obtained by reaction of $W_2(NMe_2)_6$ with Pr^{i}OH in pyridine; cf. M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. Little, and P. E. Fanwick, *Inorg. Chem.*, submitted for publication. The structure is analogous to that found for $Mo_2(OSiMe_3)_6(HNMe_2)_2$ by M. H. Chisholm, F. A. Cotton, M. W. Extine, and W. W. Reichert, *J. Am. Chem. Soc.*, **100,** 153 (1978).

(10) (a) M. J. Bennett, J. V. Brencic, and F. A. Cotton, *Inorg. Chem.*, **8,** 1060 (1969); (b) F. A. Cotton, B. A. Frenz, and Z. C. Mester, *Acta Crystallogr., Sect. B*, **29,** 1515 (1973); (c) F. A. Cotton and B. J. Kalbacher, *Inorg. Chem.*, **15,** 522 (1976).

(11) A. Bino and F. A. Cotton, *Angew. Chem.*, In press.

(12) A W═W bond with a length of 2.530 (2) Å has recently been reported by A. Bino, F. A. Cotton, Z. Dori, and J. C. Sekutowski, *Inorg. Chem.*, **17,** 2946 (1978). Re═Re bonds have long been known in $Re_3X_9L_3$-type compounds and have bond lengths of ~2.47 Å; cf. M. J. Bennett, F. A. Cotton, and B. M. Foxman, *Inorg. Chem.*, **7,** 1563 (1968), and earlier papers cited therein.

(13) We thank the Office of Naval Research and the National Science Foundation for support at Indiana and Princeton Universities and the Robert A. Welch Foundation for support at the Texas A&M University. M.H.C. was an Alfred P. Sloan Foundation Fellow, 1976–1978.

Minoru Akiyama, Dorothy Little
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Malcolm H. Chisholm,* Deborah A. Haitko
Department of Chemistry, Indiana University
Bloomington, Indiana 47405

F. Albert Cotton,* Michael W. Extine
Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received January 22, 1979

The "Supershort" Chromium-to-Chromium Quadruple Bond: Its Occurrence in a Tetracarboxamidatodichromium(II) Compound

Sir:

Extensive studies on tetracarboxylatodichromium(II) compounds[1,2] have shown that they all have Cr-Cr distances in the range 2.29-2.53 Å.[3] The closely related $[Cr_2(CO_3)_4]^{4-}$ ion has a slightly shorter distance,[1c] 2.22 Å. These rather long distances have provoked controversy as to the Cr—Cr bond order.[4,5] On the other hand, there are a number of Cr_2 species in which the Cr—Cr distances are short enough that there has been no lack of agreement that they contain quadruple bonds. While two of these (with Cr—Cr distances in parentheses), namely, $[Cr_2(CH_3)_8]^{4-}$ (1.98 Å)[6] and $Cr_2(C_3H_5)_4$ (1.97 Å),[7] have been known for several years, they are so different, at least superficially, from the $Cr_2(O_2CR)_4$ type that their general significance is (or was) ambiguous. A distinct dichotomy was created with the discovery[8] of a series of compounds, beginning with **1**, of which those in Table I are representative. These contain ligands that are sterically and electronically similar to the carboxylato group, and yet they have vastly shorter Cr—Cr bonds, i.e., in a range ≤1.90 Å, which we informally designate *supershort*.[9]

Table I. Representative Dichromium(II) Compounds Having Supershort Bonds and Their Cr—Cr Bond Lengths

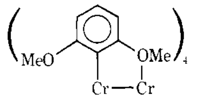
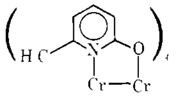
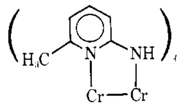
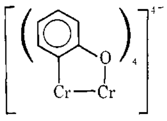
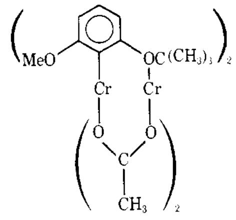
compd	no.	bond length, Å	ref
	**1**	1.85	8a
	**2**	1.89	8b
	**3**	1.87	8c
	**4**	1.83	8d
	**5**	1.86	8e

Table II. Some Bond Distances (Ångstroms) and Angles (Degrees) in $Cr_2[PhNC(CH_3)O]_4$

Cr—Cr	1.873 (7)	Cr′-Cr-O	98.0 (2)
Cr—N	2.06 (1)	Cr′-Cr-N	92.5 (3)
Cr—O	1.97 (1)		

Our attempts to identify the ligand properties responsible for the occurrence of supershort $Cr\overset{4}{-}Cr$ bonds have involved, inter alia, the following steps. (1) Compounds of type **2** (Table I) showed that the presence of Cr—C bonds is not critical, and compound **3** shows that Cr—O bonds are not essential. In short, no one type of ligand atom, C, N, or O, is critical. (2) Compound **5** showed that four noncarboxylato ligands are not necessary. (3) Compound **4** showed that it is not necessary for the Cr_2L_4 species to be a neutral molecule. (4) The one remaining common feature of all of the compounds in Table I with supershort $Cr\overset{4}{-}Cr$ bonds, namely, the incorporation of some ligand atoms in aromatic rings, was recently shown not to be essential by the discovery of supershort bonds in the compounds $Cr_2[(CH_2)_2P(CH_3)_2]_4$ (1.89 Å)[10] and $Cr_2(PhNNNPh)_4$ (1.86 Å).[11]

We report here a further crucial experimental step, perhaps the penultimate one, in achieving an understanding of what causes (or allows) the formation of supershort $Cr\overset{4}{-}Cr$ bonds. We have prepared the first carboxamido-bridged dichromium compound, viz., $Cr_2[RC(O)NR']_4$ with R = CH_3 and R′ =