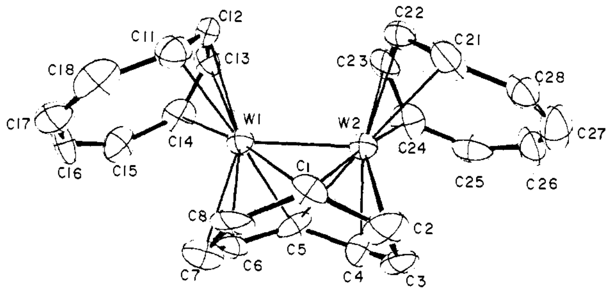

Figure 1. The molecular structure of $W_2(C_8H_8)_3$. In this ORTEP drawing each atom is represented by a scaled outline of its ellipsoid of thermal vibration.

Regrettably, the carbon atom positions,[12] and hence all the molecular parameters except the W-W distance have relatively large esds (e.g., 0.04 Å for C-C) because the intensities of all reflections are so dominated by the contribution of the tungsten atoms. Nonetheless, as shown in Figure 1, the molecular structure is of the same type as that reported for $Cr_2(C_8H_8)_3$ and the bonding can be viewed in the same way.

The bond order is believed to be 4 (as also suggested for the Cr compound[10]) because the diamagnetism requires it to be either 4 or 2, and a double bond would be expected to be much longer (Cf. 2.48-2.50 Å for Re=Re bonds).

The quadruple W-W bond in this case has a length of 2.375 (1) Å, which is ~0.12 Å longer than that in the $[W_2Me_{8-x}Cl_x]^{4-}$ ion. The length of the quadruple Cr-Cr bond in $Cr_2(C_8H_8)_3$, 2.214 (1) Å, exceeds that in the $Cr_2Me_8{}^{4-}$ ion,[13] 1.980 (5) Å, by an even greater amount.

We see here further examples of the fact that, for these M-M multiple bonds, bonds of a given order may vary considerably in length as the character of the ligands changes. It is notable that the quadruple W-W bond here is actually longer than the triple W-W bonds in the many W_2X_6 ($X = CH_2SiMe_3, NR_2$) compounds and their derivatives[14] recently described. The lengths of multiple M-M bonds seem to depend in part on the number of electrons formally occupying the orbitals of each metal atom. Thus, the $M_2X_8{}^{4-}$ ions contain 16-electron species (and the metal atoms in W_2X_6 molecules have only 12 electrons), whereas in the $M_2(C_8H_8)_3$ molecules (as well as the $CpM(CO)_2{\equiv}M(CO)_2Cp$ molecules, which have relatively long triple bonds[15]) we are dealing with 18-electron cases.

The ^{13}C and ^1H NMR spectra of $W_2(C_8H_8)_3$ at ambient temperature each contain one intense, sharp line for the 16 carbon or hydrogen atoms of the two η^4-C_8H_8 rings, which are evidently "whizzing" as rings so bound are well known to do.[16] However, we also see signals for the third ring that are consistent with its being stereochemically rigid. These observations are in contrast to the report by Timms and Turney[17] (who recently reported the preparation of $Cr_2(C_8H_8)_3$ by a metal vapor reaction) that the ^{13}C and ^1H spectra each consisted of only one resonance.[18]

Note Added in Proof. A neutron diffraction study, with J. M. Williams and A. Schultz, Argonne National Laboratory, is nearly complete, and has fully confirmed and extended the results of the x-ray work.

Supplementary Material Available: Tables of positional and thermal parameters and bond distances and angles (3 pages). Ordering information is given on any current masthead page.

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Exceedingly Short Metal-to-Metal Multiple Bonds

Sir:

Over the past decade, a facet of transition-metal chemistry first recognized[1-3] only in the early 1960s, namely, the ability of transition metal atoms to form multiple bonds, has experienced vigorous (lately, exponential) growth.[4] This growth has been highlighted by the discovery of hundreds of compounds containing triple and quadruple bonds[5] and by the development of an increasingly sophisticated understanding of the nature of these bonds.[6-9]

A natural question in this connection is how short may such multiple M-M bonds be? In terms of directly measured bond lengths in isolable compounds the shortest such bonds so far reported are to be found in several chromium[10] compounds, where Cr-Cr distances of 1.96-1.98 Å are found, and in several dimolybdenum compounds,[10] where Mo-Mo distances of ~2.09 Å are found.

Astonishingly short as these distances may seem, they are by no means the shortest possible. We report here the preparation and structural characterization of analogous dichromium and dimolybdenum compounds in which there are M-M distances that are *substantially* shorter than those mentioned above.

The reaction of 2,6-dimethoxyphenyllithium, (DMP-Li) with $Cr_2(O_2CCH_3)_4$ followed by suitable workup allows the isolation, in good yield, of red-orange and red crystalline products. These products are thermally stable at ambient temperature and only moderately air sensitive. They are crystallographically isomorphous and belong to space group $Pn2_1a$ with $Z = 4$ and the following unit cell dimensions: for $Cr_2(C_8H_9O_2)_4$, $a = 16.266$ (3), $b = 16.560$ (3), $c = 11.350$ (1) Å; for $Mo_2(C_8H_9O_2)_4$, $a = 16.576$ (3), $b = 16.436$ (5), $c = 11.546$ (3) Å. The chemical compositions are confirmed by the successful solution and refinement of the crystal structures.[11a]

The molecular structure of the chromium compound is shown in Figure 1. No crystallographic symmetry is imposed on the molecule, but it has approximately C_{2h} symmetry. Each DMP ligand is bidentate and bridging and they are arranged

Table I. Mean Values[a] of Some Important Bond Lengths (Å) and Angles (Degrees) in $Cr_2(DMP)_4$[b]

Length	Å	Angle	Degrees
Cr-Cr	1.847 (1)	Cr-Cr-C	91.1 ± 0.3
Cr-C	2.066 ± 0.010	Cr-Cr-O	101.7 ± 0.4
Cr-O	2.136 ± 0.005	C-Cr-C	91.4 ± 0.8
		C-Cr-O	166.8 ± 0.3
		C-Cr-O	91.4 ± 0.9
		O-Cr-O	83.0 ± 0.6

[a] Averaged according to the virtual C_{2h} symmetry. Error intervals are mean deviations from the mean. [b] For the Mo analogue, the Mo-Mo distance is 2.064 (1) Å.

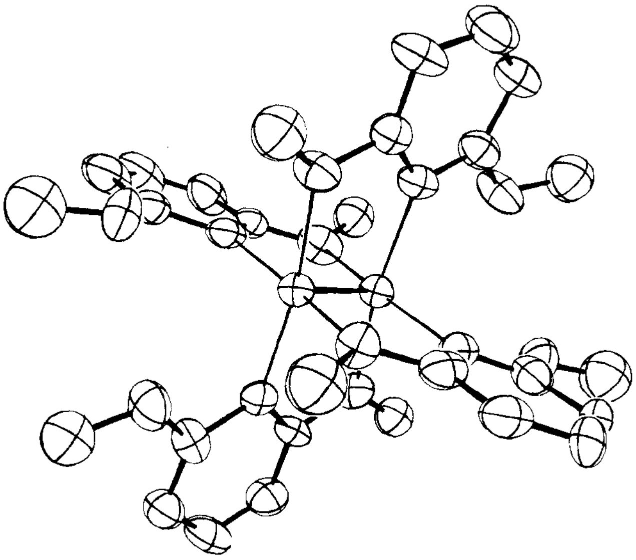

Figure 1. An ORTEP drawing of the $Cr_2(DMP)_4$ structure. The $Mo_2(DMP)_4$ structure is closely similar.

so that two adjacent DMPs project their "unused" methoxy groups over one axial position, and the other two unused MeO groups project over the other one. These projecting MeO groups very effectively block these positions to any extramolecular donors. Several of the more important bond distances and angles[11b] are listed in Table I.

The Cr-Cr and Mo-Mo distances, 1.847 (1) and 2.064 (1) Å, respectively, rivet one's attention. In the metallic elements the M-M distances are, respectively, 2.50 and 2.73 Å, and the shortest previously reported Cr-Cr and Mo-Mo distances are, respectively, ~0.11 and ~0.02 Å longer than these. All other distances found in these structures are quite normal.

In attempting to consider the significance of these new, short M-M bonds in relation to the entire body of data on short M-M bonds, it became clear that some method is needed for putting data for different metals on a common scale. In some way the length of a given M-M′ bond must be normalized with respect to the intrinsic sizes of the metal atoms, M, M′, composing it. One practical, convenient way to do this is to use Pauling's metallic radii,[12] R_1, to scale the observed distances. Thus, for homonuclear bonds, $d_{M-M}/2R_1(M)$ values should allow a comparison of relative shortness of bonds involving a diversity of metal atoms. In Figure 2 are plotted a few such data; the lower on the vertical scale, the greater the "formal shortness" so to speak, of the M-M bond.

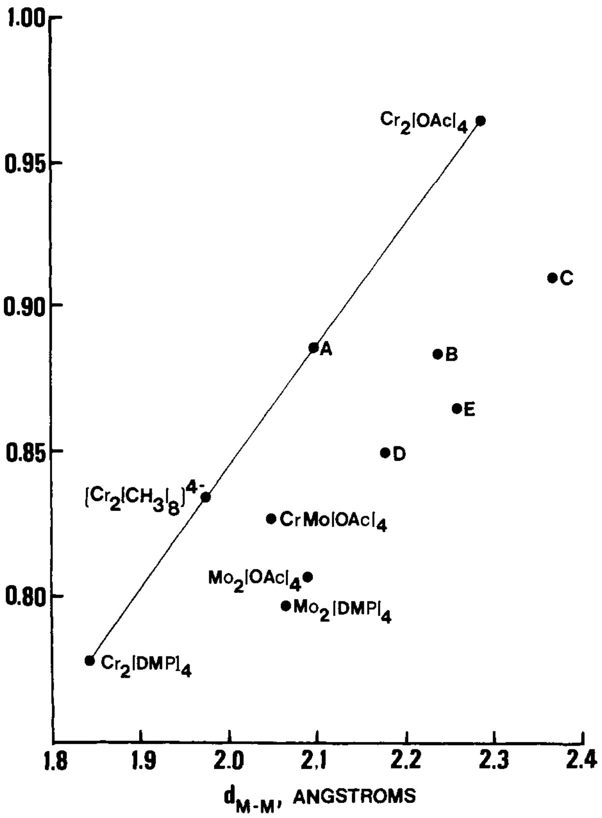

Figure 2. The absolute and formal shortness of various M-M multiple bonds. The enormous range covered by quadruple Cr-Cr bonds is apparent. The shortest Re-Re and W-W bonds, in $Re_2Me_8^{2-}$ and $W_2(CH_2SiMe_3)_6$, as well as several other representative examples are shown: A, $Cr_2(C_8H_8)_3$; B, $Re_2Cl_8^{2-}$; C, $W_2(C_8H_8)_3$; D, $Re_2(CH_3)_8^{2-}$; E, $W_2(CH_2SiMe_3)_6$.

It is evident that both of the new M-M bond lengths break all previous records for formal as well as absolute shortness, and by considerable margins. The new criterion of formal shortness also points up many interesting comparisons. For example, the formal shortness (FS) of this quadruple Cr-Cr bond is less than that of *any* other known homonuclear bond, however strong. The three strongest homonuclear bonds for which bond energies are known are triple N-N (946 kJ mol^{-1}), triple C-C (813 kJ mol^{-1}), and triple P-P (490 kJ mol^{-1}). These have FS ratios of 1.10/1.40 = 0.786, 1.206/1.54 = 0.783, and 1.89/1.10 = 0.860, respectively, all of which are, at least slightly, greater than the FS ratio of 0.778 for this new quadruple Cr-Cr bond. It may be seen in Figure 2 that for the quadruple Cr-Mo bond the FS ratio is 0.826, considerably greater than that for the Mo-Mo bond in the analogous (and isostructural) anhydrous acetate. Thus, even though the quadruple Cr-Mo bond is shorter than the quadruple Mo-Mo bond, it is "formally" not so short.[13]

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

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(11) (a) The structure of $Cr_2(DMP)_4$ was solved and refined using 2438 independent reflections with $I > 3\sigma(I)$ to residuals of $R_1 = 0.059$ and $R_2 = 0.080$. Data were collected at 22 °C, using graphite-monochromated Mo Kα radiation, on a Syntex P1 computer-controlled diffractometer. All computations were done on the PDP 11/45 computer at the Molecular Structure Corporation, College Station, Texas, employing the Enraf-Nonius structure determination package of Frenz and Okaya. The structure of

$Mo_2(DMP)_4$ is complete at R_1 = 0.045 and R_2 = 0.058. The correct enantiomorph has been found in each case. (b) A complete table of atomic positional and thermal parameters is available as supplementary material. See paragraph at end of paper for ordering information.

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(13) Support from the National Science Foundation is gratefully acknowledged.

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Primary and Tertiary Amines as Catalysts of Hydrogen Transfer in the Photocyclization of 1,1-Diarylethylenes

Sir:

In a previous communication we have shown that 1-(α-naphthyl)-1-phenylethylene (I) yields 1-phenylacenaphthylene (II) by irradiation in the presence of iodine and oxygen.[1] In the absence of the oxidant, direct irradiation of a degassed cyclohexane solution of I slowly leads to a mixture of II and 1-phenylacenaphthene (III).[2] This cyclization is not triplet sensitized (nor quenched by oxygen) and it might therefore be ascribed to a short-lived species such as the S_1 state.[3]

We were interested to know whether the formation of exciplexes or radical ions from the interaction of photoexcited I with amines would favor or inhibit the photocyclization to III. We have found that addition of amines[4] to a degassed cyclohexane solution of I accelerates the photocyclization of I to give III as the almost exclusive product. We wish to report here[6] the preliminary results of a study of the scope of the reaction and of the mechanism of this unprecedented catalysis of a photocyclization by amines.

1. Scope of the Reaction. A number of experiments, summarized in Table I, were performed to test the potential synthetic value of this reaction which generates five-membered carbocyclic rings. The cyclization proceeds with high yield with R = Ph or CN, if it involves an α-naphthyl or 1-pyrenyl aromatic nucleus. The failure of reactions 7–9 originates, probably, from unfavorable electronic interactions for the cyclization. Diaminoalkanes are the most effective catalysts.

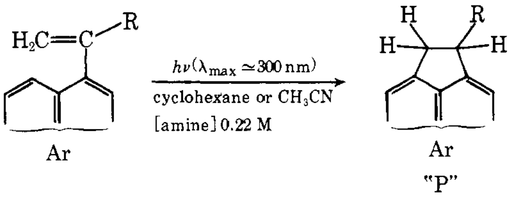
2. Mechanism. The simplest and best documented system was 1-(α-naphthyl)-1-phenylethylene (I) which was used as a model.

Quantum yields were measured at 313 nm in standard conditions described in Table II, with valerophenone as actinometer.[7]

When their alkyl groups are not too bulky, tertiary amines are efficient catalysts of the photocyclization; for example, Et_3N and Dabco increase the quantum yield ϕ_{III}, respectively, $\simeq$20 times and $\simeq$40 times relative to the uncatalyzed reaction, but n-Pr_3N is far less efficient. These amines are known to be good quenchers of the fluorescent state of arenes. As expected, I gives a fluorescent exciplex with Et_3N in cyclohexane[8], λ_{max} 440 nm. The Stern–Volmer plot for the amine quenching of monomer fluorescence gives $k_q\tau = 4.63\ M^{-1}$. The S_1 lifetime τ of I in cyclohexane was measured[9] to be $\tau = 1.2 \times 10^{-9}$ s from which we derive $k_q = 3.86 \times 10^9\ M^{-1}\ s^{-1}$.

The formation of an exciplex is not sufficient to induce a catalytic effect, since dimethyl sulfide and 1,3-cyclohexadiene, which are efficient quenchers of S_1 states of arenes and have a lower ionization potential than primary alkylamines,[11] do not catalyze the reaction. Moreover, the quenching of the S_1 state of I is not a prerequisite to the reaction: with 1,3-diaminopropane in acetonitrile (at concentrations up to 0.22 M) the monomer fluorescence is not measurably quenched, whereas the quantum yield ϕ_{III} is 0.39 at [1,3-diaminopropane] of 0.22 M. These results indicate that there is no relation between the ionization potential and the effectiveness of the catalyst. On the contrary, the catalytic capacity appears to correlate with the basicity. The diaminoalkanes, which are the most effective amines have much higher gas-phase basicities than primary amines.[12] Even if the difference is less in solution, the monoprotonated forms of these amines exist largely as cyclic internally hydrogen-bonded species even in water.[13] Pyridine, which is slightly basic, does not catalyze the cyclization.

Table I[a]



Expt	Ar	R	Sol-vent	Amine	"P" yield, %
1	α-Naphthyl	Ph	CH	Et_3N	80
2	α-Naphthyl	Ph	CH	n-$PrNH_2$	90
3	α-Naphthyl	Ph	AN	n-$PrNH_2$	95
4	4-Methoxy (α-naphthyl)	Ph	CH	Et_3N	70
5	5-Acenaphthenyl	Ph	CH	Et_3N	85
6	1-Pyrenyl	Ph	CH	$NH_2(CH_2)_3NH_2$[b]	60
7	9-Phenanthryl	Ph	CH	$NH_2(CH_2)_3NH_2$[b]	0[c]
8	5-Chrysenyl	Ph	CH	$NH_2(CH_2)_3NH_2$[b]	0[c]
9	3-Fluoranthenyl	Ph	CH	$NH_2(CH_2)_3NH_2$[b]	0[c]
10	α-Naphthyl	α-Naphthyl	CH	$NH_2(CH_2)_3NH_2$[b]	85
11	α-Naphthyl	CH_3	CH	$NH_2(CH_2)_3NH_2$[b]	0
12	α-Naphthyl	CN	CH	$NH_2(CH_2)_3NH_2$[b]	95

[a] Irradiation were carried out with a Rayonet with RUL lamps: $\lambda_{max} \simeq 300$ nm; exposure time $\simeq$3 h (expt 1–5), 18 h (expt 6–12); CH = cyclohexane, AN = acetonitrile. [b] The diamine is not completely miscible with CH. [c] Extended irradiation gives rise to the reduction of the double bond.

Table II. Quantum Yields of Formation of II and III by Irradiation (313 nm) of I (5×10^{-3} M) in Cyclohexane (CH) or Acetonitrile (AN) in the Presence of Electron Donors (0.22 M)

Electron donors	Solvent	ϕ_{II}[a]	ϕ_{III}[a]
None	CH	0.014 ± 0.005	0.005 ± 0.002
	AN	0.008 ± 0.002	0.002 ± 0.001
	CH[b]	0.03 ± 0.003	$\leqslant$0.001
Et_3N	CH	0.02 ± 0.003	0.12 ± 0.02
	AN	0.004 ± 0.001	0.26 ± 0.02
	CH[b]	0.13 ± 0.02	$\leqslant$0.001
n-$PrNH_2$	CH	0.01 ± 0.002	0.11 ± 0.02
Dabco (0.0125 M)	CH	0.02 ± 0.004	0.22 ± 0.02
$NH_2(CH_2)_3NH_2$	CH[c]	0.007 ± 0.002	0.31 ± 0.02
	AN	$\leqslant$0.001	0.39 ± 0.04
$NH_2(CH_2)_4NH_2$	CH[c]	0.006 ± 0.002	0.34 ± 0.02
Pyridine	CH	0.003 ± 0.002	0.005 ± 0.002
Me_2S	CH	0.009 ± 0.002	0.002 ± 0.001
	CH	0.006 ± 0.002	$\leqslant$0.001

[a] Degassed solutions by four freeze and thaw cycles. The amount of II and III formed after 1–4% (CH) or 5–11% (AN) conversion is determined by VPC. Valerophenone is used as actinometer.[7] [b] Air saturated. [c] The diaminoalkanes are not completely miscible with CH.

Other bases, KOH or K_2CO_3 (0.22 M) in $MeOH$-H_2O (4:1 v/v), increase ϕ_{III} about three times. Since the media are different, one cannot compare the efficiencies of catalysis of bases in aqueous methanol with those of amines in cyclohexane.