The precise mechanism of the carbometalation reported here is not yet clear. However, our preliminary investigation has revealed that the product **1** in the reaction of phenylacetylene with Me₃Al-Cl₂ZrCp₂ is largely an (*E*)-2-phenylpropenyl-alane species (~95%) mixed with a minor amount (~5%) of the corresponding organozirconium species. Thus, the ¹H NMR spectrum of the phenylacetylene-Me₃Al-Cl₂ZrCp₂ reaction mixture in CH₂Cl₂ shows two distinct allylic methyl signals at δ 2.35 and 1.93 ppm in the ratio of ~20:1. The ¹H NMR spectra of authentic samples of **5** and **6** prepared by
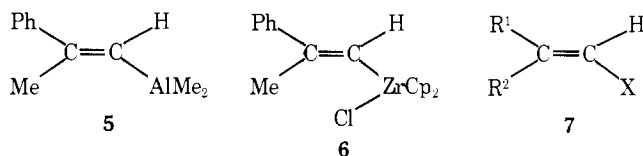
treating **4** with *n*-BuLi, followed by addition of Me₂AlCl and Cl₂ZrCp₂, respectively, show their allylic signals at δ 2.35 and 1.93 ppm, respectively. These results not only support the above conclusion, but indicate the following. (1) The interconversion between the organoaluminum and organozirconium species is slow on the NMR time scale, in contrast to the methyl exchange. (2) The propenyl C-1 atom in the products is not bonded simultaneously to both Al and Zr to any detectable extent. The spectroscopic data presented above suggested that the carbometalation reaction might be catalytic with respect to Cl₂ZrCp₂. Indeed, the reaction of 1 equiv of phenylacetylene with 2 equiv of Me₃Al in the presence of 0.1 equiv of Cl₂ZrCp₂ for 12 h at 25 °C produced, after hydrolysis, α-methylstyrene in 60% yield.

While the scope and the mechanistic details remain to be further explored, it is clear that a novel, selective, and operationally simple route to trisubstituted olefins represented by **7** via carbometalation of R¹C≡CH is now at our disposal. Various known reactions of alkenylaluminums,[24] including those reported in the accompanying communication,[20] point to the potential utility of the alkenyl metal products obtainable by the procedure reported here in the synthesis of trisubstituted olefins.

Reference and Notes

(1) Selective Carbon–Carbon Bond Formation via Transition Metal Catalysis. 8. Part 7: N. Okukado, D. E. Van Horn, W. L. Klima, and E. Negishi, *Tetrahedron Lett.*, in press.
(2) For a review, see H. C. Brown, "Hydroboration", W. A. Benjamin, New York, N.Y., 1962.
(3) For a review, see T. Mole and E. A. Jeffery, "Organoaluminum Compounds", Elsevier, Amsterdam, 1972.
(4) (a) For a review, see E. Ya. Lukevits and M. G. Voronkov, "Organic Insertion Reactions of Group IV Elements", Consultant Bureau, New York, N.Y., 1966. (b) For a paper on Pt-catalyzed hydrosilylation of acetylenes, see R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *J. Am. Chem. Soc.*, **83**, 4385 (1961).
(5) (a) A. J. Leusink, H. A. Budding, and J. W. Marman, *J. Organomet. Chem.*, **9**, 285, 295 (1967). (b) E. J. Corey and R. H. Wollenberg, *J. Am. Chem. Soc.*, **96**, 5582 (1974); *J. Org. Chem.*, **40**, 2265 (1975).
(6) For a review, see J. Schwartz, *J. Organomet. Chem. Libr.*, **1**, 461 (1976).
(7) (a) For carboalumination of internal acetylenes at elevated temperatures, see ref 3. (b) For the addition reaction of vinylmagnesium halides to alkynols, see H. G. Richey and F. W. von Rein, *J. Organomet. Chem.*, **20**, P32 (1969). (c) For the carbotitanation of alkynols, see R. A. Coleman, C. M. O'Doherty, H. E. Tweedy, T. V. Harris, and D. W. Thompson, *ibid.*, **107**, C15 (1976). (d) For a photochemical reaction of Cp₂TiMe₂ with diphenylacetylene and bis(pentafluorophenyl)acetylene, see W. H. Boon and M. D. Rausch, *J. Chem. Soc., Chem. Commun.*, 397 (1977). (e) For the carborhodation of diphenylacetylene, see M. Michman and M. Balog, *J. Organomet. Chem.*, **31**, 395 (1971). (f) For the addition reaction of MeMgBr-Cl₂Ni(PPh₃)₂ with internal acetylenes, see J.-G. Duboudin and B. Jousseaume, *ibid.*, **44**, C1 (1972). (g) Although no references are given here, a variety of allylic organometallics react with acetylenes to form the corresponding addition products.

(8) (a) J. F. Normant and M. Bourgain, *Tetrahedron Lett.*, 2583 (1971). (b) For a review, see J. F. Normant, *J. Organomet. Chem. Libr.*, **1**, 219 (1976).
(9) H. Westmijze, J. Meijer, H. J. T. Bos, and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, **95**, 304 (1976).
(10) Reference 3a, p 410, and references cited therein.
(11) The reaction takes place even when 1 equiv of Me₃Al is used. However, the yield of 2-methyl-1-octene is 70–80%.
(12) Obtained from Ethyl Corp.
(13) (a) J. R. Surties, *Chem. Commun.*, 567 (1965); (b) P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organomet. Chem.*, **33**, 181 (1971).
(14) P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organomet. Chem.*, **34**, 155 (1972).
(15) A detailed NMR study is being carried out.
(16) Sadtler NMR Catalog No. 9908.
(17) Prepared by treating phenylacetylene with 1.2 equiv of *n*-BuLi at <−50 °C followed by deuterolysis.
(18) Satisfactory spectroscopic data have been obtained.
(19) Reference 3a, p 270.
(20) E. Negishi, N. Okukado, A. O. King, D. E. Van Horn, and B. I. Spiegel, *J. Am. Chem. Soc.*, following paper in this issue.
(21) (a) R. B. Bates, D. M. Gale, and B. J. Bruner, *J. Org. Chem.*, **28**, 1086 (1963); (b) J. W. K. Burrell, R. F. Garwood, L. M. Jackman, E. Oskay, and B. C. L. Weedon, *J. Chem. Soc.*, 2144 (1966).
(22) Our attempts to prepare the same product by the reaction of (*E*)-1-iodo-2-methyl-1-hexene with LiCu(Bu-*n*)₂ in a manner similar to that reported for analogous transformations (E. J. Corey and G. H. Posner, *J. Am. Chem. Soc.*, **90**, 5615 (1968)) resulted in the formation of the desired product only in <5% yield.
(23) Efforts are being made to overcome these difficulties.
(24) (a) Reference 3a; (b) G. Bruno, "The Use of Aluminum Alkyls in Organic Synthesis", Ethyl Corp., Baton Rouge, La.; (c) G. Zweifel, *Intra-Sci. Chem. Rept.*, **7**, 181 (1973); (d) E. Negishi, *J. Organomet. Chem. Libr.*, **1**, 93 (1976).

David E. Van Horn, Ei-ichi Negishi*
Department of Chemistry, Syracuse University
Syracuse, New York 13210
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Double Metal Catalysis in the Cross-Coupling Reaction and Its Application to the Stereo- and Regioselective Synthesis of Trisubstituted Olefins[1]

Sir:

We have recently developed highly selective procedures for the synthesis of olefins which involve the reaction of alkenylalanes or alkenylzirconium derivatives (**1**) with unsaturated organic halides in the presence of a Pd⁰-phosphine or Ni⁰-phosphine complex.[2] While these procedures offer a facile entry into certain disubstituted olefins,[2] our initial attempts to apply them to the synthesis of trisubstituted olefins via **2** were unsuccessful or unsatisfactory. Particularly frustrating was the generally low reactivity of **3**, which is now readily available via carbometalation as described in the accompanying communication,[1] in the Pd-catalyzed cross-coupling.

R, R¹, or R² = alkyl; MLₙ = Al< or ZrCp₂Cl
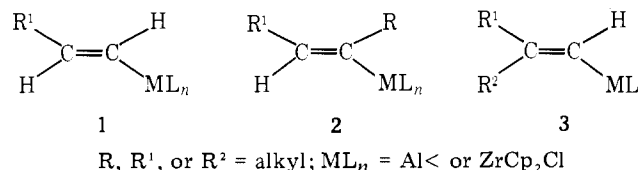
To alleviate this difficulty, we turned our attention to a simple but little-tested possibility of doubly or multiply catalyzing the Pd- or Ni-catalyzed cross-coupling reaction[3] which presumably proceeds via oxidative addition–transmetalation–reductive elimination.[4] Since the difficulty appeared largely steric in orgin, and since steric acceleration rather than steric hindrance was expected in the reductive elimination step, the difficulty appeared to lie in the transmetalation step.[5] We further reasoned that, in the catalytic reaction of this nature, the difficulty must be kinetic rather than thermodynamic, and that such a kinetically unfavorable transmetalation process

Table I. The Pd- or Ni-Catalyzed Reaction of Alkenylaluminum or Alkenylzirconium Compounds with Organic Halides in the Presence of $ZnCl_2{}^a$

Alkyne	Hydrometalation or carbometalation agent	Organic halide	Product[b]	Yield,[c] %	
				GLC	Isold
3-Hexyne	*i*-Bu$_2$AlH	*m*-Tolyl iodide	(*E*)-3-(*m*-Tolyl)-3-hexene	88	
3-Hexyne	*i*-Bu$_2$AlH	**7**	**8**	65	
5-Decyne	H(Cl)ZrCp$_2$	Phenyl iodide	(*E*)-5-Phenyl-5-decene	80[d]	65
3-Hexyne	H(Cl)ZrCp$_2$	**7**	**8**	85	72
3-Hexyne	H(Cl)ZrCp$_2$	(*E*)-1-Iodo-1-hexene	(*E,E*)-4-Ethyl-3,5-decadiene	86	71
3-Hexyne	H(Cl)ZrCp$_2$	Vinyl bromide	(*E*)-3-Ethyl-1,3-hexadiene	79	62
1-Heptyne	Me$_3$Al–Cl$_2$ZrCp$_2$	Vinyl bromide	(*E*)-4-Methyl-1,3-nonadiene	73	
1-Heptyne	Me$_3$Al–Cl$_2$ZrCp$_2$	1-Iodo-1-hexyne	(*E*)-8-Methyltridec-7-en-5-yne	90	75
1-Heptyne	Me$_3$Al–Cl$_2$ZrCp$_2$	(*E*)-1-Iodo-1-hexene	(*E,E*)-8-Methyl-5,7-tridecadiene	65	
6-Methyl-5-hepten-1-yne	Me$_3$Al–Cl$_2$ZrCp$_2$	Vinyl bromide	**11**	70[e]	56
1-Heptyne	*i*-Bu$_2$AlH	1-Iodo-1-hexyne	(*E*)-Tridec-7-en-5-yne	92	

^{a} All reactions were run at 20–25 °C under an atmosphere of nitrogen in the presence of 1 equiv of $ZnCl_2$. Unless otherwise mentioned, $Pd(PPh_3)_4$ was used as a catalyst (5 mol %). ^{b} All isolated products have been adequately characterized and identified by ^1H and ^{13}C NMR and IR. The stereoselectivity in each case is $\geq$97% by GLC and ^1H and ^{13}C NMR. ^{c} The yields of homo-coupled products were 0–5% each. ^{d} $Ni(PPh_3)_4$ was used as a catalyst (10 mol %). ^{e} The Pd catalyst obtained by treating $Cl_2Pd(PPh_3)_2$ with 2 equiv of *i*-Bu$_2$AlH was used (5 mol %).

could be facilitated by the use of one or more coordinatively unsaturated compounds of low steric requirements containing metals whose electronegativities are either comparable with or between those of the two metals in question, i.e., Al or Zr and Pd or Ni. Conceptually, a single transmetalation process of high activation energy could be replaced by a double or multiple transmetalation process of low kinetic barriers, which could lead to an overall rate enhancement. We therefore tested various metal salts containing Cu, Zn, Cd, In, Sn, and Ti.[6]

We now report that many of the Pd- or Ni-catalyzed reactions of the alkenylaluminum or -zirconium compounds represented by **1-3** with alkenyl, aryl, or alkynyl halides, which either fail to give or produce only in low yields the cross-coupled products, can be significantly promoted to give the desired products in high yields by the addition of metal salts containing Zn or Cd, such as $ZnCl_2$. Thus, for the first time, the Pd- or Ni-catalyzed cross-coupling reaction represented by eq 1


$$1\text{-}3$$
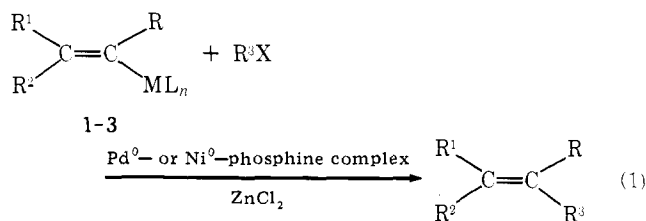
R, R^1, or R^2 = H or alkyl; R^3 = alkenyl, aryl or alkynyl; ML$_n$ = Al< or ZrCp$_2$Cl; X = Br or I

provides a generally applicable procedure capable of producing various trisubstituted olefins. Although the scope of the current discussion is restricted to the synthesis of olefins, the concept of double or multiple metal catalysis presented here promises to prove useful in various cross-coupling and other types of organometallic reactions.

Typically, the reaction of (*E*)-3-hexenyldiisobutylalane (**4**) with *m*-iodotoluene in the presence of 5 mol % of $Pd(PPh_3)_4$ did not produce any more than a trace (<1%) of (*E*)-3-(*m*-tolyl)-3-hexene (**5**) even after 1 week at room temperature.[7] This reaction was chosen as a test system, and the effect of various metal salts was examined. Whereas InI_3, $SnCl_4$ or $TiCl_4$[8] did not induce the formation of **5** in any appreciable yields (<5%) within 48 h, the addition of 1 equiv of $ZnCl_2$ or

$CdCl_2$ resulted in a dramatic rate enhancement ($>10^4\times$), the desired product **5**[9] being formed in 88 or 76% yield, respectively, within 1 h at room temperature. As no cross-coupling takes place in the absence of the Pd or Ni catalysts, the reaction is promoted by both the Pd or Ni complexes and $ZnCl_2$ or $CdCl_2$. Although much less effective, CuI (1 equiv) induced the formation of **5** in 36% yield in 24 h at room temperature. We have therefore tentatively chosen $ZnCl_2$ as a cocatalyst in all subsequent cases.

That the action of $ZnCl_2$ is indeed catalytic has been shown in the reaction of **6** with **7** in the presence of 5 mol % of


6   **7**

8 ($\geq$97% *E,E*)
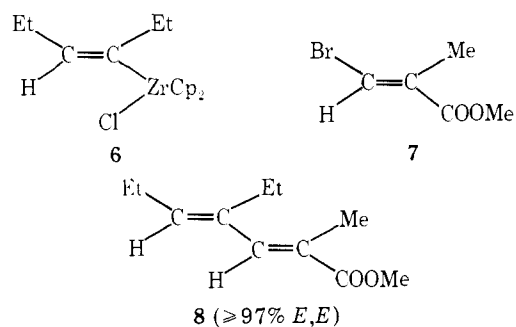
$Pd(PPh_3)_4$. Thus, the use of 1, 0.5, and 0.2 equiv of $ZnCl_2$ induced the formation of **8**[9] in 82 (1 h), 85 (1 h) and 72% (2 h) yields, respectively, in the indicated periods, whereas essentially no product (<2%) was formed in the absence of $ZnCl_2$ even after 6 h, at which time almost all of **7** had been consumed in some side reaction.

The experimental results obtained by using $ZnCl_2$ as an added reagent are summarized in Table I. It should be emphasized that, in the absence of $ZnCl_2$, the reactions in Table I either fail to produce the desired products in appreciable yields or are far more sluggish than the $ZnCl_2$ promoted reactions.

Particularly attractive from the viewpoint of natural products synthesis is the stereoselective one-pot conversion of terminal acetylenes into conjugated dienes (**9**) and enynes[10] (**10**) via **3** (R^2 = Me), as exemplified by the transformation shown in eq 2. Although the carbometalation of terminal acetylenes
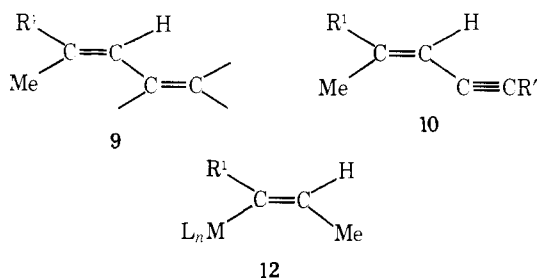
with $Me_3Al-Cl_2ZrCp_2$ produces 95:5 mixtures of two regioisomers,[1] the cross-coupled products obtained by using a minor excess (10%) of the alkenyl metal intermediates are regiochemically >99% pure, indicating that the alkenyl metal species represented by **3** (R^2 = Me) are considerably more reactive in the cross coupling than their regioisomers represented by **12**. Attempts are being made to further convert the conjugated dienes **9**, such as **11**, and enynes **10** into various natural products.

$$70\% \; 11^9 \; (\geqslant 98\% \, E) \qquad (2)$$
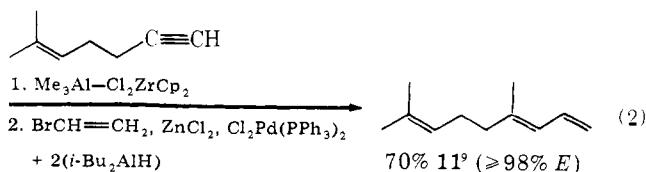
Although the exact role of $ZnCl_2$ remains to be clarified, the possible intermediacy of alkenylzinc species has been indicated by the observation that the formation of (E)-8-methyltridec-7-en-5-yne (**10**, R^1 = Pent-n; R' = Bu-n) in the reaction of (E)-2-methyl-1-heptenylzinc chloride[11] with 1-iodo-1-hexyne is at least as fast as that in the $ZnCl_2$ promoted reaction of **3** (R^1 = Pent-n; R^2 = Me) with 1-iodo-1-hexyne.

References and Notes

(1) Selective Carbon–Carbon Bond Formation via Transition Metal Catalysis. 9. Part 8: The accompanying paper, D. E. Van Horn and E. Negishi, *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) (a) E. Negishi and S. Baba, *J. Chem. Soc., Chem. Commun.*, 596 (1976); (b) S. Baba and E. Negishi, *J. Am. Chem. Soc.*, **98**, 6729 (1976); (c) E. Negishi and D. E. Van Horn, *J. Am. Chem. Soc.*, **99**, 3168 (1977); (d) N. Okukado, D. E. Van Horn, W. L. Klima, and E. Negishi, *Tetrahedron Lett.*, in press.

(3) For a recent paper containing pertinent references, see E. Negishi, A. O. King, and N. Okukado, *J. Org. Chem.*, **42**, 1821 (1977).

(4) This mechanistic scheme was proposed by Kumada (K. Tamao, K. Sumitani, and M. Kumada, *J. Am. Chem. Soc.*, **94**, 4374 (1972)) for the Ni-catalyzed cross-coupling reaction, and has been supported by Parshall (G. W. Parshall, *ibid.*, **96**, 2360 (1974)) and Kochi (D. J. Morrell and J. K. Kochi, *ibid.*, **97**, 7262 (1975)).

(5) The oxidative addition step does not involve the organometallic compound added as a carbon group transfer agent.

(6) The Allred–Rochow electronegativity values (A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958)) for the metals used in this study including Pd and Ni are as follows: Pd (1.35), Ni (1.75), Al (1.47), Zr (1.22), Cu (1.75), Zn (1.66), Cd (1.46), In (1.49), Sn (1.72) and Ti (1.32).

(7) The corresponding reaction of (E)-1-hexenyldiisobutylalane gave (E)-1-(m-tolyl)-1-hexene in 75% yield in 12 h at 25 °C. A similar sluggish reaction of an (E)-2-octenylzirconium derivative with phenyl iodide was reported earlier in ref 2c.

(8) Various metals which have not been considered for different reasons include highly electropositive group 1a and 2a metals, highly electronegative metals of relatively small sizes (B, Si, etc.) and heavy metals (Hg, Tl, Pb, etc.) whose salts are readily reducible by Pd^0 or Ni^0 complexes.

(9) All isolated products have been adequately characterized and identified by ^1H and ^{13}C NMR and IR.

(10) A similar enyne synthesis via β,β-dialkyl-substituted alkenylcoppers has been reported recently (J. F. Normant, A. Commercon, and J. Villieras, *Tetrahedron Lett.*, 1465 (1975)). Although no difficulty was encountered in reproducing some of the reported results, our attempts to apply the procedure to the synthesis of dienes using alkenyl iodides, such as (E)-1-iodo-1-hexene, instead of alkynyl iodides have been almost totally un-

successful, no more than traces of the desired cross-coupled products being produced.

(11) Prepared by treating (E)-1-iodo-2-methyl-1-heptene[1] with n-BuLi (-78 °C) and $ZnCl_2$.

Ei-ichi Negishi,* Nobuhisa Okukado, Anthony O. King
David E. Van Horn, Barry I. Spiegel
Department of Chemistry, Syracuse University
Syracuse, New York 13210
Received November 28, 1977

Reactions of Triply Bonded Dimetal Compounds. Reversible Addition of Carbon Monoxide to a Hexakis(alkoxy)dimolybdenum Compound. A Molecule with a Carbonyl-Bridged Metal–Metal Double Bond

Sir:

We report here our initial observations on a series of most remarkable reactions involving carbon monoxide and $Mo_2(OR)_6$ compounds, which contain unbridged metal–metal triple bonds.[1]

Alkane solutions of $Mo_2(OR)_6$ compounds, where R = Me_3C, Me_2CH, and Me_3CCH_2, rapidly absorb carbon monoxide at room temperature to give dark solutions.[2] Upon exposure to 2 equiv of CO, crystalline compounds have been obtained merely by cooling the alkane solutions to ca. -10 °C. Black crystalline compounds of empirical formula $Mo(OR)_3CO$ have been obtained[3] for R = Me_2CH and Me_3CCH_2 and a preliminary x-ray investigation has shown that the isopropoxide is tetranuclear, $Mo_4(OPr^i)_{12}(CO)_4$. The IR spectrum of the latter compound shows four well-resolved and sharp bands of approximately equal intensity assignable to coordinated carbonyl ligands: 1957, 1882, 1837, and 1819 cm^{-1}. When R = Me_3C, a dark purple crystalline compound, $Mo_2(OBu^t)_6CO$ (**I**) was obtained which showed only one IR band, at 1670 cm^{-1}, assignable to a carbonyl group.

All the new carbonyl compounds are thermally labile. **I** readily loses CO on heating in vacuo and $Mo_2(OBu^t)_6$ is recovered. Carbon monoxide is also lost in solution under a nitrogen purge or under vacuum. This establishes the reversibility of reaction 1 below.

$$Mo_2(OBu^t)_6 + CO \rightleftarrows Mo_2(OBu^t)_6CO \qquad (1)$$

The black crystalline compounds, $Mo_4(OR)_{12}(CO)_4$, where R = Me_2CH and Me_3CCH_2, yield $Mo(CO)_6$ at 50 °C (10^{-2} Torr) and $Mo_2(OR)_8$ compounds at 80-100 °C (10^{-2} Torr). Other nonvolatile products are as yet uncharacterized in these thermal decomposition reactions.

Upon exposure to an excess of CO (1 atm), $Mo_2(OR)_6$ compounds react further. For example, after exposing a hexane solution of $Mo_2(OBu^t)_6$ to an excess of CO (1 atm) for 12 h, the solvent was stripped, leaving a black powdery residue which showed the following IR bands assignable to carbonyl groups: 2022 (m), 1985 (vs), four overlapping bands at ~1930 (all strong), 1830 (w), 1690 (vw), 1670 (w), and 1630 (w) cm^{-1}. The band at 1985 cm^{-1} is assignable to $Mo(CO)_6$ and, even at room temperature (1 atm), this compound slowly sublimes out of the black residue. Thus it appears that formation of **I** represents merely the first step in a chain of reactions which leads to $Mo(CO)_6$ among other as yet uncharacterized products. We proceeded directly toward a full structural characterization of the novel carbonyl compound (**I**).

Crystals of **I** consist of discrete dinuclear molecules with the structure shown in Figure 1. Here we omit, for the sake of clarity, the $(CH_3)_3C$ groups. Each molecule possesses a crystallographically[4] imposed mirror plane containing O1, C1, O2, and O3 and bisecting the Mo–Mo bond. The virtual symmetry of the molecule is C_{2v}. The coordination polyhedron about each