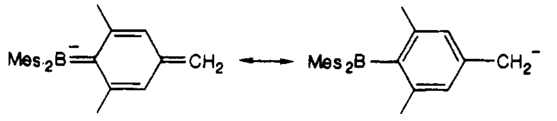
(1)C(1)C(10)C(19) in which the B(1)–C(1) length 1.522 (10) Å averages 0.087 Å (5.4%) shorter than either B(1)–C(10), 1.615 (12) Å, or B(1)–C(19), 1.602 (11) Å. In the C(1) ring, C(2)–C(3) and C(3)–C(6) are both 1.362 (10) Å and are significantly shorter than the other ring C–C distances and the C–C lengths in the remaining mesityl rings. The exocyclic, para C(4)–C(8) bond 1.349 (10) Å is also much shorter than the corresponding distance in the ether solvated benzyllithium complex $[(\mathrm{Li(Et_2O)CH_2C_6H_5})_\infty]$, 1.432 (1) Å.[9] These distances suggest a significant contribution to the structure of **1** by canonical form **1a**. Since the carbanion center in **1b** has little or no protection from the 3,5 Me groups, it appears that the stability of **1** is due mainly to delocalization rather than steric effects.



1a **1b**

The B(1)–C(1) bond length 1.522 (10) Å also merits further comment. It is significantly shorter than those seen in trialkyl- or triarylboranes.[10] A number of recent publications have referred to boron carbon multiple bonds as part of various cyclic systems.[11,12] The only X-ray structural determination involves the 1,3-dihydro-1,3-diborete $\mathrm{Me_2N}\overline{\mathrm{B{-}C(}t\mathrm{{-}Bu){-}B(NMe_2){-}C}}(t\mathrm{{-}Bu})$. This also features shortened B–C bond lengths of 1.501 (5) and 1.503 (5) Å.[13] These are consistent with calculations which consider the four-membered $\overline{-\mathrm{BCBC}-}$ ring as an aromatic 2π-electron system isoelectronic with the [cyclobutadiene]$^{2+}$ cation.[14] It appears then that the B(1)–C(1) moiety in **1** is the first structurally characterized example of an exocyclic B–C multiple bond. Further evidence for the formulation of B(1)–C(1) as multiple bond may be seen in (i) the angles at B(1) which involve a much smaller C(10)B(1)C(19) angle, 111.6 (6)°, than the other two which have values of 123.5 (7)° and 124.9 (8)° and (ii) the low dihedral angle of 25.8° between the near planar core B(1)C(1)C(10)C(19) and the C(1) ring. This is much smaller than the typical dihedral of ca. 50° seen in BMes$_3$[15] and BMeMes$_2$[16] or the other dihedral angles in **1** of 56.3° for C(1) ring and 52.9° for the C(19) mesityl ring.

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Registry No. $[\mathrm{Li(12\text{-}crown\text{-}4)_2}][\mathrm{CH_2C_6H_2(3,5\text{-}Me_2)(4\text{-}B\{2,4,6\text{-}Me_3C_6H_2\}_2)}]\cdot\mathrm{Et_2O}$, 103712-53-4.

Supplementary Material Available: Summary of data collection and refinement and tables of atom coordinates and thermal parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (9 pages); a listing of structure factors (16 pages). Ordering information is given on any current masthead page.

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[9] Beno, M. A.; Hope, H.; Olmstead, M. M.; Power, P. P. *Organometallics* **1985**, *4*, 2117.

[10] Odom, J. D. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982, Vol. 1, p 238.

[11] van der Kerk, S. M.; Budzelaar, P. H. M.; van der Kern-van Hoof, A.; van der Kerk, G. M.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 48. Bock, H.; Roth, B.; Maier, C. B. *Chem. Ber.* **1984**, *117*, 172. Broxterman, Q. B.; Hogeveen, H. *Tetrahedron Lett.* **1983**, 639. Courtneige, J. L.; Davies, A. G.; Lusztyke, E.; Lusztyk, J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 155.

[12] Wehrmann, R.; Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 369. Wehrmann, R.; Pues, C.; Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 372. Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 877.

[13] Hildebrand, M.; Pritzkow, H.; Zennech, U.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 371.

[14] Cremer, D.; Gauss, J.; Schleyer, P. v. R.; Budzelaar, P. H. M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 370. Schleyer, P. v. R.; Budzelaar, P. H. M.; Cremer, D.; Kraka, E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 374.

[15] Blount, J. F.; Finocchario, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7019.

[16] Bartlett, R. A.; Power, P. P., unpublished results.

Photoactivation of Methyl Acetate by Chromium Atoms

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Summary: Photolysis of the cocondensate of methyl acetate and chromium vapor yields a complex that decomposes to acetaldehyde and formaldehyde.

The advent of metal vapor synthesis during the past decade provides an important new method for the preparation of certain organometallic species that are difficult to synthesize by more traditional routes.[1] Metal atoms are in a state of "ultimate coordinative unsaturation" and are highly reactive. However, in any metal vapor reaction there is always a major competing reaction—metal atom recombination to form metal clusters and particles. If the desired metal atom/substrate reaction has a significant activation barrier, then clustering may become the dominant reaction at the low temperatures required by the technique unless the substrate has a significant ability to adduct with the metal atoms. Even then, there has been no convenient method of imparting the addition energy into the system needed to make the reaction proceed.

Photolysis has often been used in matrix isolation spectroscopy as a way of introducing additional energy into the systems studied.[2-5] Photoexcitation of macroscale metal vapor reactions promises to be a similiarly useful method of producing new chemistry. We report here the results of a study on the photoactivation of methyl acetate by chromium atoms using a metal vapor reactor.[6]

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[1] The following books and review articles give an overview of metal vapor chemistry. (a) Timms, P. L. In *Cryochemistry*; Moskovits, M., Ozin, G. A., Eds.; Wiley: New York, 1976; pp 61–134. (b) McGlinchey, M. J.; Skell, P. S. *Ibid.*; pp 135–194. (c) Blackborow, J. R.; Young, D. *Metal Vapor Synthesis in Organometallic Chemistry*; Springer-Verlag: Berlin, 1979. (d) Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic: New York, 1980. (e) Timms, P. L. *Adv. Inorg. Chem. Radiochem.* **1972**, *14*, 121. (f) Timms, P. L.; Turney, T. W. *Adv. Organomet. Chem.* **1977**, *15*, 53. (g) Klabunde, K. J. *Acc. Chem. Res.* **1975**, *8*, 393. (h) Shriver, D. F. *Inorg. Synth.* **1979**, *19*, 59.

[2] Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7393.

[3] Ozin, G. A.; McIntosh, D. F.; Mictchell, S. A. *J. Am. Chem. Soc.* **1981**, *103*, 1574.

[4] Ozin, G. A.; McCaffrey, J. G. *J. Am. Chem. Soc.* **1982**, *104*, 7351.

[5] Ozin, G. A., McCaffrey, J. G. *Inorg. Chem.* **1983**, *22*, 1397.

[6] Howard and Miles have used a similar device in their ESR studies.[7,8] Ours is a true preparative device, while theirs is a microscale matrix isolation device.

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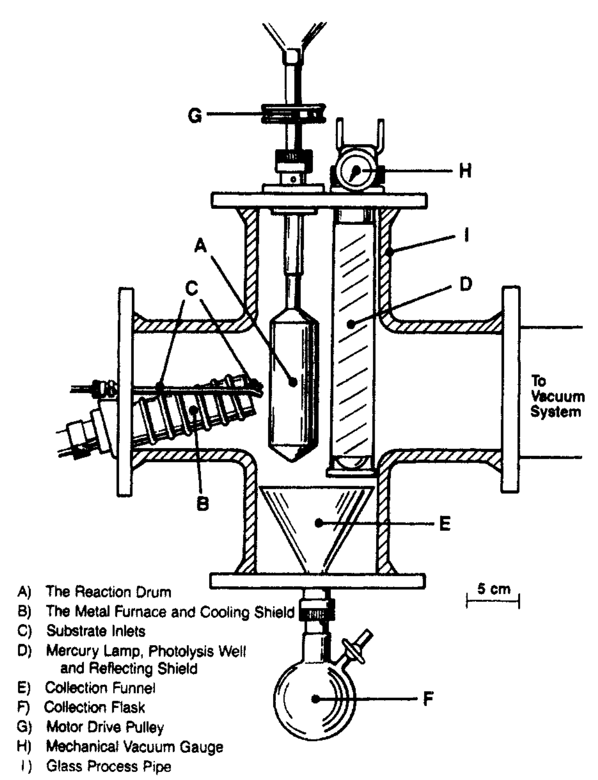
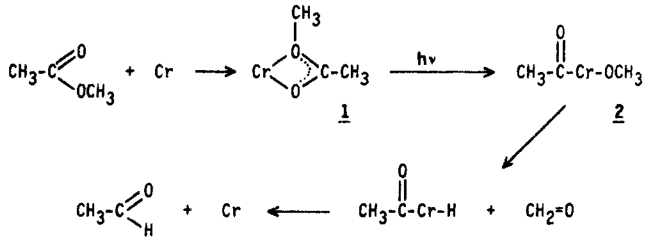


Figure 1. Photochemical metal vapor reactor.

Scheme I



The reactor used in this study is illustrated in Figure 1. This apparatus may be used to cocondense metal vapor with any sufficiently volatile organic compound onto a stainless-steel drum at 77 K. The drum is rotated during the cocondensation to assure that the cocondensate is uniformly deposited. Photolysis is carried out during the cocondensation using a 450-W medium-pressure Hg arc lamp. All reactions are carried out at 10^{-5} torr. Products may be readily collected in the receiving flask as the matrix is allowed to warm.

When the cocondensate of methyl acetate and chromium vapor is photolyzed, the major organic product is acetaldehyde. Under the most favorable conditions (700/1 molar ratio of ester to metal) acetaldehyde is produced in a 60% yield (based on metal deposited).[9] Several other minor products are isolated from the reaction including methanol, methyl formate, and formaldehyde. Cocondensation of the ester with chromium vapor in the absence of photolysis yields only trace amounts of methanol and methyl formate. A thermal reaction of excess methyl acetate with the metal clusters and particles formed upon warmup would account for the formation of methanol and methyl formate; this appears to be a minor reaction pathway in both cases.

An attractive rationalization of the photoformation of acetaldehyde and formaldehyde in this system is illustrated in Scheme I. The formation of adduct 1 has been demonstrated at 15 K by using matrix isolation spectroscopy where cocondensation of chromium and methyl acetate producted clearly discernible shifts in the carbonyl and C–O stretching frequencies.[10] The existence of a stable ligated metal species at 77 K can be shown by the fact that the same products are producted if the reactants are first cocondensated and then the matrix is photolyzed. The extremely high organic to metal ratio required for this reaction clearly indicates that a metal atom reaction is occurring. Photoinsertion of the chromium atom into the $C{-}OCH_3$ bond of the adducted ester would form intermediate **2**. Decomposition of **2** by β-hydride transfer[11] and reductive elimination[12] would then yield acetaldehyde and formaldehyde in equimolar quantities; the low observed yield of formaldehyde may be accounted for by its difficulty of isolation. Photolytic cocondensation of chromium and methyl acetate-d_3 yields acetaldehyde-d_3 as predicted by this mechanism.

Other acetate esters also react with chromium vapor to yield acetaldehyde, but the efficiency of the reaction drops dramatically as the size of the alkyl group is increased.

We are continuing to investigate the photolytic reactions of metal atoms with other organic compounds, and the results of these studies will be reported later.

Acknowledgment. We gratefully acknowledge the 3M Co. for support of this work.

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[7] Buck, A. J.; Mile, B.; Howard, J. A. *J. Am. Chem. Soc.* 1983, *105*, 3381.

[8] Howard, J. A.; Sutcliffe, R.; Tse, J. S.; Mile, B. *Organometallics* 1984, *3*, 859.

[9] Over a 3-h period 0.36 mmol of chromium was condensed with 256 mmol of methyl acetate. Volatile products were identified by GC and GC/MS using a Porapak QS column. The yield of acetaldehyde was determined by using benzene as an internal standard.

(10) Methyl acetate and chromium vapor were codeposited with excess argon onto a copper surface. Stretching frequencies were determined by using a Beckman IR-9 infrared spectrometer. The carbonyl and C–O stretching frequencies of adduct 1 were measured as 1687 and 1110 cm^{-1}, respectively, compared to 1799 and 1252 cm^{-1} for free methyl acetate.

(11) β-Hydride shifts in metal–methoxyl compounds have been observed. Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc. Dalton Trans.* 1977, 1546.

(12) (a) Milstein, D. *Organometallics* 1982, *1*, 1549. (b) Azran, J.; Orchin, M. *Organometallics* 1984, *3*, 197.

Direct Synthesis of Low-Valent Acyl Isocyanide Metal Complexes. Preparation, Structure, and Properties of $(\eta^5\text{-}C_5H_5)Co(CNCOR)_2$ Complexes Formed via Reaction of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ with Acyl Isocyanides

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Summary: Compounds $(\eta^5\text{-}C_5H_5)Co(CNCOR)_2$, R = C_6H_5 (Ia) and 1-adamantyl (Ib), have been prepared, Ia for the first time and Ib in improved yield, by displacement of CO from $(\eta^5\text{-}C_5H_5)Co(CO)_2$ by CNCOR at ambient temperature. This exceptionally easy complete displacement of CO is attributed to the strong π-acceptor character of the acyl isocyanide ligand.

The acyl isocyanide ligand $:C{\equiv}NC({=}O){-}R$ has been shown, by its effect on carbonyl ligand stretching fre-