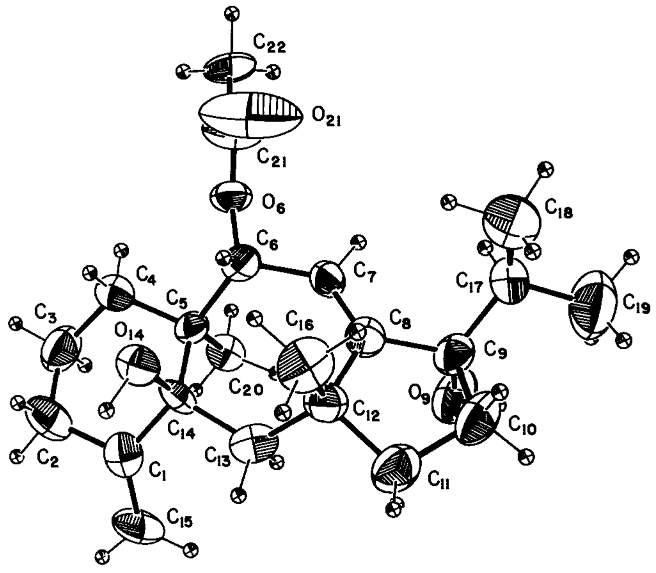


Figure 1.

The perspective view shown in Figure 1 displays the essential conformational features of the molecule. Since the absolute configuration has not been determined only the relative configuration can be shown.

While diterpenes with an angular 6-7-5 ring system such as phorbol (**2**) are characteristic of the Euphorbiaceae plant family,[8] dolatriol represents the first member of a hitherto unknown linear system.[9,10] Also of interest in respect to dolatriol is the allylic positioning of each oxygen substituent.

The detailed structural features of this molecule as well as the unusual packing scheme will be discussed in a complete presentation of the structure. Evaluation of dolatriol and related substances from *Dolabella* species is presently in progress.

Acknowledgments. For support of this investigation we are grateful to the National Cancer Institute, National Institutes of Health (performed pursuant to Contract No. N01-CM-12308 with the Division of Cancer Treatment, NCI, Department of Health, Education and Welfare), Public Health Research Grant No. CA-16049-02 from the National Cancer Institute, the Fannie E. Rippel Foundation, the J. W. Kieckhefer Foundation, Talley Industries, the Phoenix Coca-Cola Bottling Company, Mr. E. Romley, the Ladies Auxiliary VFW, Department of Arizona, and Mrs. A. O. Jones. The calculations for the structure analysis were performed with computer time provided by Arizona State University, and we also wish to thank Mr. L. Vanell for assistance with several experiments.

References and Notes

(1) Contribution 46 in the series Antineoplastic Agents. For Part 45 refer to G. R. Pettit, C. L. Herald, and D. L. Herald, Jr., *J. Pharm. Sci.*, in press.

(2) L. H. Hyman, "The Invertebrates. Mollusca I", American Museum of Natural History, McGraw-Hill, New York, N.Y., 1967.

(3) Cf. B. W. Halstead, "Poisonous and Venomous Marine Animals of the World", Vol. 1, U.S. Government Printing Office, Washington, D.C. 1965, p 709.

(4) T. Higa and P J. Scheuer, *J. Am. Chem. Soc.*, **96**, 2245 (1974).

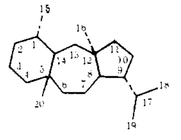
(5) Three such species are in the *Aplysia* genus, namely, *angasi* (South Pacific, Australia), *californica* (Gulf of California, Mexico) and *dactylomela* (Indian Ocean, East Africa). See also, G. R. Pettit, J. F. Day, J. L. Hartwell, and H. B. Wood, *Nature* (*London*), **227**, 962 (1970). Several interesting halogenated substances have already been isolated from *Aplysia dactylomela* and *californica:* F. J. McDonald, D. C. Campell, D. J. Vanderah, F. J. Schmitz, D. M. Washecheck, J. E. Burks, and D. van der Helm, *J. Org. Chem.*, **40**, 665 (1975); F. J. Schmitz and F. J. McDonald, *Tetrahedron Lett.*, 2541 (1974); D. J. Faulkner, M. O. Stallard, J. Fayos, and J. Clardy, *J. Am. Chem. Soc.*, **95**, 3413 (1973), and M. O. Stallard and D. J. Faulkner, *Comp. Biochem. Physiol. B*, **49**, 37 (1974).

(6) M. H. J. Koch, *Acta Crystallogr., Part A*, **30**, 67 (1974); J. P. Declerq, G. Germain, P. Main, and M. M. Woolfson, *ibid.*, **29**, 231 (1973); G. Germain, P. Main, and M. M. Woolfson, *ibid.*, **27**, 368 (1971).

(7) All calculations other than data reduction and direct methods were performed with the "CRYSTALS" computing package adapted to the UNIVAC 1110: R. S. Rollett and J. R. Carruthers, personal communication.

(8) Y. Hirata, *Pure Appl. Chem.*, **41**, 175 (1975), M. Hergenhahn, W. Adolf, and E. Hecker, *Tetrahedron Lett.*, 1595 (1975), and S. M. Kupchan, I. Uchida, A. R. Branfman, R. G. Dailey, Jr., and B. Y. Fei, *Science*, **191**, 571 (1976).

(9) We recommend that the hydrocarbon system of this new class of diterpenes be designated dolastane and numbered as illustrated in structure i.



i

(10) Interestingly, some of the phorbol-type diterpenes are very toxic and cocarcinogenic. L. Crombie, M. L. Games, and D. L. Pointer, *J. Chem. Soc. C*, 1347 (1968). More recently two members of this series have been found to display antineoplastic activity: M. S. Kupchan, I. Ucheda, A. R. Branfman, R. G. Dailey, Jr., and B. Yu Fei, *Science*, **191**, 571 (1976).

George R. Pettit,* Richard H. Ode, Cherry L. Herald
Robert B. Von Dreele, Claude Michel
Cancer Research Institute and Department of Chemistry
Arizona State University
Tempe, Arizona 85281

Received April 12, 1976

An Acylsilane Derivative of a Transition Metal

Sir:

The physical and chemical properties of acylsilanes, acylgermanes, and acylstannanes are known to differ markedly from those of their carbon analogues.[1-4] As an extension of our interest in transition metal-group 4 chemistry, we have undertaken the preparation of group 4 acyl derivatives of transition metals. We report here the synthesis and characterization of the first transition metal bonded acylsilane, *fac*-$Re(CO)_3(diphos)[C(O)SiPh_3]$ (**1**).

Compound **1** was prepared by adding a THF solution of Ph_3SiLi[5] to a slurry of $[Re(CO)_4(diphos)][ClO_4]$[6] (**2**) in THF at 25°. After 90 min, the mixture was concentrated and treated with acetone to precipitate the crude product, which was then recrystallized from methylene chloride-acetone to yield air-stable purple crystals of **1** in 25-30% yield.[7] Upon melting (182-184°), **1** decolorizes and evolves CO, and the mass spectrum, obtainable only above 180°, corresponds to that of the product of thermal decarbonylation *mer*-$Re(CO)_3(diphos)SiPh_3$.

Samples of ^{13}C enriched **1** for spectroscopic studies were prepared using two enrichment procedures. In one, $Re(CO)_5Cl$

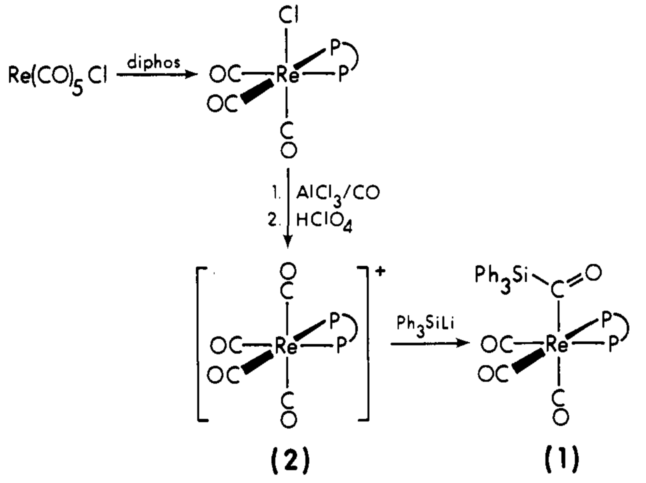


Table I. Spectral Properties of *fac*-$Re(CO)_3(diphos)[C(O)SiPh_3]$ (**1**) and Related Acyls

	ν (acyl CO)[a] (cm^{-1})	λ_{max} (ϵ)[b]	^{13}C NMR[c] (δ Me_4Si)
1	1490	557 (3.9×10^2)[d]	340.1
$Ph_3SiC(O)SiPh_3$	1558[e]	554[e,f]	—
$Ph_3SiC(O)Ph$	1614	424 (2.9×10^2)	230.7
$PhC(O)Ph$	1654	345 (1.3×10^2)	196.4[g]

[a] KBr pellet. [b] CCl_4 solvent except as noted; most intense low energy absorption. [c] CD_2Cl_2 except as noted. [d] CH_2Cl_2 solvent. [e] Reference 12a. [f] Light sensitive; ϵ could not be accurately determined. [g] $CDCl_3$ solvent; ref 14.

was enriched in CH_2Cl_2 solution by uv irradiation in the presence of ^{13}CO. More conveniently, ^{13}CO could be introduced by preparing **2** at 60° under a ^{13}CO pressure of a few atmospheres.[8] As determined by ^{13}C NMR and ir, the entering ^{13}CO *stereospecifically* assumes an axial position.[9] The ^{13}C spectra of **1** are consistent with its formation primarily by nucleophilic attack of Ph_3Si^- at an axial carbonyl carbon of **2**.[10]

Since an assignment for the acyl carbonyl stretching vibration could not be made by inspection of the ir spectrum (KBr pellet) of unenriched **1**, the spectra of a series of enriched samples were obtained. A comparison of these spectra enabled assignment of this mode to a very weak band at 1490 cm^{-1} that was nearly coincident with one of several strong aromatic absorptions in the region. Confirmation of this assignment was obtained from the Raman spectra, in which a single strong band was observed at 1485 cm^{-1} in the unenriched solid, and bands at 1485 and 1450 cm^{-1} in an enriched sample. This vibration occurs at lower energies than normally observed in the ir spectra of rhenium acyl species (1562–1645 cm^{-1})[11] or related acylsilanes[12] (Table I). This value suggests high electron density on the acyl oxygen atom, and is in fact in a region more normally associated with transition metal acylate species.[13] Through a similar ir spectral comparison, the Si–C(acyl) stretching vibration was assigned at 786 cm^{-1} (m).

The ^{13}C NMR chemical shift of the acyl carbon atom in **1** is 340.1 ppm downfield from Me_4Si. This carbon atom is deshielded strongly with respect to $Ph_3SiC(O)Ph$ (Table I) and the rhenium acyls $Re(CO)_5C(O)R$ (R = Ph, δ 245.4; R = Me, δ 244.0).[14] It is also more strongly deshielded than the carbene carbons in $[Me_2GeRe(CO)_4COMe]_2$ (δ 305.7)[14,15] and *cis*-$Me_3GeRe(CO)_4C(OEt)Me$ (δ 314.8).[14]

Unlike other rhenium acyls,[11] **1** has prominent electronic transitions centered in the visible region, with the most intense low energy absorption at 557 nm. In Table I are listed λ_{max} data for the corresponding bands[16] of related compounds. Dramatic increases in λ_{max} values have also been reported upon substitution of silyl moieties for R in other heteroatom-containing chromophores,[17] including RN=NR[18] and $RN{=}CR'_2$.[19] We offer no explanation at this time for the observation of very similar λ_{max} values for **1** and $Ph_3SiC(O)SiPh_3$.[20]

LCAO-MO theory of ^{13}C NMR shielding suggests that the paramagnetic shielding of a carbon atom is inversely related to ΔE, the mean excitation energy.[21] Correlations have been drawn between ^{13}C NMR shifts and λ_{max} values (as an approximation to $(\Delta E)^{-1}$). Thus, for organic carbonyl compounds, increased deshielding accompanied increased electronic transition wavelengths.[22] From the values in Table I, we suggest the possibility of similar extended trends for acylsilanes.

Acknowledgment. We wish to thank the National Research Council of Canada for financial support and for a Postdoctorate Fellowship (to J.R.A., 1974–1976).

References and Notes

(1) A. G. Brook, *Acc. Chem. Res.*, **7**, 77 (1974).

(2) A. G. Brook, *Adv. Organomet. Chem.*, 7, 95 (1968).

(3) G. J. D. Peddle, *J. Organomet. Chem.*, **14**, 139 (1968).

(4) A. G. Brook, J. B. Pierce, and J. M. Duff, *Can. J. Chem.*, **53**, 2874 (1975).

(5) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958); H. Gilman, D. J. Peterson, and D. Wittenberg, *Chem. Ind. (London)*, 1479 (1958).

(6) E. W. Abel and S. P. Tyfield, *Can. J. Chem.*, **47**, 4627 (1969).

(7) Anal. ($C_{48}H_{39}O_4P_2ReSi$) C, H, O. Infrared spectrum in CH_2Cl_2: 2007(s), 1924(s), 1915(s, sh). A number of related experiments have yielded products with infrared spectra similar to that of **1**. In a future publication we will discuss the properties of these products, which are in general less stable than **1** and difficult to isolate free of starting cation.

(8) The procedure is a modification of the reported preparation of *trans*-$[Re(CO)_4(PPh_3)_2][PF_6]$ under a CO pressure of 1 atm: R. J. Angelici and R. W. Brink, *Inorg. Chem.*, **12**, 1067 (1973). A 1:2 molar ratio of *fac*-$Re(CO)_3(diphos)Cl$ and anhydrous $AlCl_3$ in benzene was heated at 60° under a few atmospheres of ^{13}CO. After 60 min, the solvent was removed and the residue extracted with cold aqueous methanol. The product was precipitated with perchloric acid and recrystallized from methanol–ether to yield stereospecifically axially enriched **2** (85%).

(9) The ^1H and ^{31}P decoupled ^{13}C NMR of nonstereospecifically enriched **2** has resonances at 182.9 and 184.1 ppm downfield from Me_4Si (−60°, CD_2Cl_2 solvent). In the ^{31}P coupled spectrum, these resonances appear as a triplet (J_{PC} = 8 Hz, axial CO) and a doublet of doublets (J_{PC} = 41 and 8 Hz, equatorial CO), respectively. The latter resonance is not observed in stereospecifically enriched **2**.

(10) The ^1H and ^{31}P decoupled ^{13}C NMR of **1**, when prepared from nonstereospecifically enriched **2**, has resonances at 340.1 (acyl C), 194.6, and 196.1 ppm downfield from Me_4Si (30°, CD_2Cl_2 solvent). In the ^{31}P coupled spectrum, these resonances appear as a triplet (J_{PC} = 10 Hz), a triplet (J_{PC} = 6 Hz, CO trans to acyl), and a doublet of doublets (J_{PC} = 50 and 9 Hz, CO trans to P), respectively. When prepared from stereospecifically axially enriched **2**, the enrichment in **1** appears mainly in the first two sites.

(11) W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.*, **94**, 862 (1961); E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1962).

(12) (a) A. G. Brook, P. F. Jones, and G. J. D. Peddle, *Can. J. Chem.*, **46**, 2119 (1968); (b) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *J. Am. Chem. Soc.*, **82**, 5102 (1960).

(13) W. O. Siegl and J. P. Collman, *J. Am. Chem. Soc.*, **94**, 2516 (1972); E. O. Fischer and V. Kiener, *J. Organomet. Chem.*, **23**, 215 (1970).

(14) M. J. Webb, Ph.D. Thesis, University of Alberta, 1975.

(15) M. J. Webb, M. J. Bennett, L. Y. Y. Chan, and W. A. G. Graham, *J. Am. Chem. Soc.*, **96**, 5931 (1974).

(16) These transitions have normally been assigned as n → π^*; however, the assignment $\sigma \rightarrow \pi^*$ has recently been proposed for acylsilanes: B. G. Ramsey, A. Brook, A. R. Bassindale, and H. Bock, *J. Organomet. Chem.*, **74**, C41 (1974).

(17) B. G. Ramsey, "Electronic Transitions in Organometalloids", Academic Press, New York, N.Y., 1969, Chapter 4.

(18) H. Bock, K. Wittel, M. Veith, and N. Wiberg, *J. Am. Chem. Soc.*, **98**, 109 (1976), and references therein.

(19) L.-H. Chan and E. G. Rochow, *J. Organomet. Chem.*, **9**, 231 (1967).

(20) In contrast to solutions of $Ph_3SiC(O)SiPh_3$, solutions of **1** are stable in light, but decolorize upon ultraviolet irradiation. Other transitions occur at 670 (10) and 383 nm (~3.4×10^3).

(21) J. A. Pople, *Mol. Phys.*, 7, 301 (1964), and references therein.

(22) D. H. Marr and J. B. Stothers, *Can. J. Chem.*, **45**, 225 (1967); G. B. Savitsky, K. Namikawa, and G. Zweifel, *J. Phys. Chem.*, **69**, 3105 (1965).

J. R. Anglin, W. A. G. Graham*
Department of Chemistry, University of Alberta
Edmonton, Alberta T6G 2E1, Canada

Received March 25, 1976

New 1,4-Diketone Synthesis Using Nitroolefins and Trimethylsilyl Enol Ethers. A Convenient Regiospecific Route to Cyclopentenones

Sir:

Despite their well-known electrophilic character, aliphatic nitroolefins have rarely been used in the Michael addition with monofunctional carbonyl compounds, probably due to the instability of the former compounds under conventional reaction conditions (strong alkaline media), while nitroolefins tolerate acidic environment. Since nitro groups are synthetically equivalent to carbonyl groups,[1] the Michael addition of this type should provide a new entry to 1,4-dicarbonyl compounds **4**,[2] which are potential precursors of conjugated cyclopentenones **5** useful for the synthesis of natural cyclopentanoids. Another advantage of this method is that a wide variety of α-, β-, and α,β-substituted nitroethylenes **2** are readily