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$_4$Si)
1	1490	557 (3.9×10^2)[d]	340.1
Ph$_3$SiC(O)SiPh$_3$	1558[e]	554[e,f]	—
Ph$_3$SiC(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$_2$Cl$_2$ except as noted. [d] CH$_2$Cl$_2$ solvent. [e] Reference 12a. [f] Light sensitive; ϵ could not be accurately determined. [g] CDCl$_3$ solvent; ref 14.

was enriched in CH$_2$Cl$_2$ 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$_3$Si$^-$ 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$_4$Si. This carbon atom is deshielded strongly with respect to Ph$_3$SiC(O)Ph (Table I) and the rhenium acyls Re(CO)$_5$C(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$_2$GeRe(CO)$_4$COMe]$_2$ (δ 305.7)[14,15] and *cis*-Me$_3$GeRe(CO)$_4$C(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$_3$SiC(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$_4$P$_2$ReSi) C, H, O. Infrared spectrum in CH$_2$Cl$_2$: 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 ^{1}H and ^{31}P decoupled ^{13}C NMR of nonstereospecifically enriched **2** has resonances at 182.9 and 184.1 ppm downfield from Me$_4$Si (−60°, CD$_2$Cl$_2$ 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 ^{1}H 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$_4$Si (30°, CD$_2$Cl$_2$ 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$_3$SiC(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).

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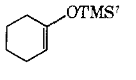
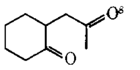
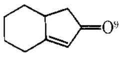
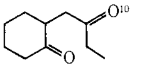
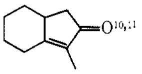
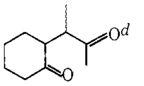
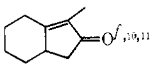
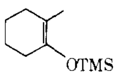
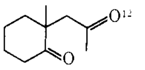
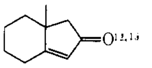
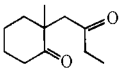
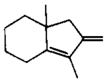
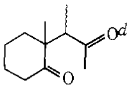
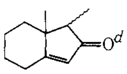
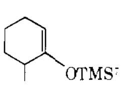
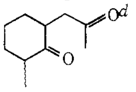
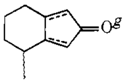
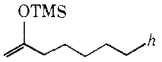
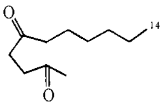
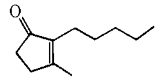
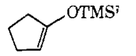
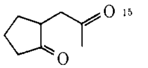
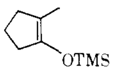
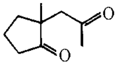
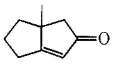
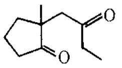
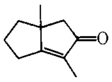
New 1,4-Diketone Synthesis Using Nitroolefins and Trimethylsilyl Enol Ethers. A Convenient Regiospecific Route to Cyclopentenones

Sir:

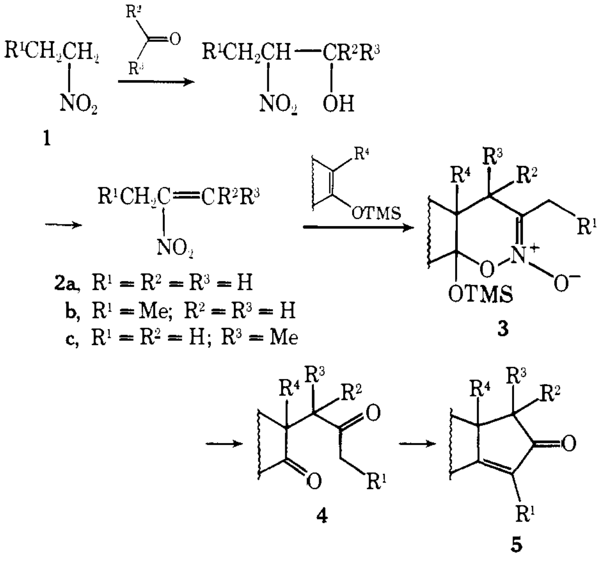
Despite their well-known electrophilic character, aliphatic nitroolefins have rarely been used in the Michael addition with monofunctional carbonyl compounds, probably due to the instability of the former compounds under conventional reaction conditions (strong alkaline media), while nitroolefins tolerate 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

Table I

Trimethylsilyl enol ether[a]	Nitroolefin	Lewis acid[b]	1,4-Diketone[a]	Yield[c] (%)	Cyclopentenone[a]	Yield[c] (%)
 [7]	2a	$SnCl_4$	[8]	85	[9]	83
	2b	$TiCl_4$	[10]	76	[10,11]	89
	2c	$AlCl_3$	[d]	63[e]	[f,10,11]	80
	2a	$TiCl_4$	[12]	70	[12,13]	93
	2b	$TiCl_4$		82		87
	2c	$SnCl_4$	[d]	71	[d]	85
 [7]	2a	$SnCl_4$	[d]	63	[g]	81
 [h]	2a	$SnCl_4$	[14]	65	[14]	80
 [7]	2a	$SnCl_4$	[15]	70[i]		—[j]
	2a	$SnCl_4$		41[k]		79
	2b	$SnCl_4$		41		88

[a] All new compounds showed the expected spectra and gave satisfactory elemental analyses. [b] Only optimum Lewis acids are listed. [c] Isolated yield. [d] Diastereomer mixture. [e] Hydrochloric acid (10%) was used for hydrolytic treatment. [f] Double bond isomerization product. [g] Mixture of double bond isomers and diastereomers. [h] This compound was prepared in 50% yield from 2-octanone by treatment with lithium diisopropylamide followed by quenching with trimethylsilyl chloride, bp 111–112° (40 mm). [i] Benzene was used as solvent. Reaction temperature was kept at 5–6° and then allowed to rise to 13°. [j] A complex mixture was produced upon standard alkaline treatment. [k] This diketone was obtained along with the corresponding nitroketone (19%), which was easily converted into the diketone in a high yield under the standard Nef reaction conditions (NaOH, then aqueous HCl).

accessible from nitroalkanes **1** via an aldol-type addition with carbonyl compounds followed by dehydration.[3] With these nitroethylenes various substituted cyclopentenones may be derivable on this annelation procedure (eq 1).



(1)

Our attention focused on the Michael addition of silyl enol ethers and nitroolefins under acidic conditions. In this reaction one can expect the formation of reaction intermediates equivalent to a nitronic acid, such as **3**, which are susceptible to hydrolysis yielding 1,4-diketones **4**. We report that when the reaction of trimethylsilyl enol ethers and nitroolefins is catalyzed by Lewis acids, 1,4-diketones are directly obtained in good yields without isolation of nitroketones or related intermediates.

2-Nitropropene[4,5] (**2a**), 2-nitro-1-butene[5] (**2b**), and 2-nitro-2-butene[5,6] (**2c**) were used as the Michael acceptors. Acyclic and alicyclic trimethylsilyl enol ethers[7] used are listed in Table I. The solvent of general use is methylene chloride. Some common Lewis acids were examined to optimize the yield in each case, and it was found that stannic chloride or titanium tetrachloride is generally best. Reaction was allowed to start at −78° and the mixture was then gradually warmed to 0°. Water was added and the mixture was refluxed to afford the 1,4-diketone which in general was the sole volatile product. The diketone formed could be purified by single distillation or short column chromatography. The isolated diketone was then submitted to alkaline aldol cyclization (KOH, aqueous EtOH, reflux) giving the cyclopentenone (see Table I).

High regiospecificity observed in the selective formation of 1,4-diketones (GLC, TLC, and NMR) demonstrates that despite the use of strong Lewis acids, no double bond migration of the silyl enol ethers takes place during the reaction with nitroolefins because of the mild reaction conditions. Ready accessibility of starting materials, high regiospecificity, good yields, and simple manipulation make the present 1,4-diketone synthesis a very useful method.

The following experimental procedure is illustrative of our 1,4-diketone synthesis. 1-Trimethylsilyloxycyclohexene[7] (170 mg, 1.0 mmol) was added dropwise to a cooled dry methylene chloride solution (−78°) of freshly distilled stannic chloride (260 mg, 1.0 mmol) and 2-nitropropene (131 mg, 1.5 mmol) over 5 min with stirring under nitrogen. The mixture was stirred at the same temperature for an additional hour and then warmed gradually to 0° over 2 h. Water (1.5 ml) was added and the resultant heterogeneous mixture was stirred at reflux for 2 h. Extraction with ethyl acetate was followed by washing with water and brine. Removal of the solvent left a residue, which was filtered through a short alumina column (Woelm, activity III) eluting with ether. Single distillation (80°, 0.2 mm) of the eluate gave pure 2-acetonylcyclohexanone[9] (131 mg, 85%).

References and Notes

(1) W. E. Norland, *Chem. Rev.*, **55**, 137 (1955); H. Shechter and F. T. Williams, Jr., *J. Org. Chem.*, **27**, 3699 (1962); A. H. Pagano and H. Shechter, *ibid.*, **35**, 295 (1970); J. E. McMurry and J. Melton, *J. Am. Chem. Soc.*, **93**, 5309 (1971); *J. Org. Chem.*, **38**, 4367 (1973); J. E. McMurry, *Acc., Chem. Res.*, 7, 281 (1974); N. Kornblum and P. A. Wade, *J. Org. Chem.*, **38**, 1418 (1973); J. E. McMurry, J. Melton, and H. Padgett, *ibid.*, **39**, 259 (1974).

(2) For recent syntheses of 1,4-dicarbonyl compounds, see G. Stork and R. Borsch, *J. Am. Chem. Soc.*, **86**, 935 (1964); G. Buchi and H. Wuest, *J. Org. Chem.*, **31**, 977 (1966); E. J. Corey and L. S. Hegedus, *J. Am. Chem. Soc.*, **91**, 4926 (1969); J. Ficini and J-P. Genet, *Tetrahedron Lett.*, 1565 (1971); J. E. McMurry and T. E. Glass, *ibid.*, 2575 (1971); J. E. McMurry and J. Melton, *J. Am. Chem. Soc.*, **93**, 5309 (1971); *J. Org. Chem.*, **38**, 4367 (1973); T. Mukaiyama, K. Narasaka, and M. Furusato, *J. Am. Chem. Soc.*, **94**, 8641 (1972); T. Mukaiyama, M. Araki, and H. Takei, *ibid.*, **95**, 4763 (1973); M. Araki, S. Sakata, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **47**, 1777 (1974); J. L. Herrmann, J. E. Richman, and R. H. Schlessinger, *Tetrahedron Lett.*, 3271 (1973); G. Stork and L. Maldonado, *J. Am. Chem. Soc.*, **96**, 5272 (1974); R. K. Boeckman, Jr., and K. J. Bruza, *Tetrahedron Lett.*, 3365 (1974); Y. Ito, T. Konoike, and T. Saegusa, *J. Am. Chem. Soc.*, **97**, 649 (1975); *ibid.*, 97, 2912 (1975); C. G. Chavdarian and C. H. Heathcock, *ibid.*, 97, 3822 (1975); R. A. Ellison, E. R. Luckenbach, and C.-W. Chiu, *Tetrahedron Lett.*, 499 (1975); M. Larcheveque, G. Valette, T. Cuvigny, and Normant, *Synthesis*, 256 (1975); R. D. Clark, L. G. Kozar, and C. H. Heathcock, *Synth. Commun.*, **5**, 1 (1975); R. K. Boeckman, Jr., and K. J. Bruza, *J. Chem. Soc., Chem. Commun.*, 519 (1975); K. Kondo and D. Tunemoto, *Tetrahedron Lett.*, 1397 (1975); T. Nakai, E. Wada, and M. Okawara, *ibid.*, 1531 (1975).

(3) For a recent review, see H. H. Bauer and L. Urbas, "The Chemistry of the Nitro and Nitroso Groups", Part 2, H. Feuer, Ed., Interscience, New York, N.Y., pp 75–117, 1970.

(4) This compound was prepared from 2-nitro-1-propanol, which was obtained, according to the reported procedure,[16] from nitroethane and formalin in 84% yield. Contrary to the literature,[17] **2a** could be stored without decomposition as low-melting crystals in a refrigerator for several months.

(5) Dehydration of nitroalcohols was carried out with phthalic anhydride.[17] The use of 1.35 equiv of the anhydride considerably improved the yields of nitroolefins, thus giving **2a**, **2b**, and **2c** from the corresponding nitroalcohols in 72, 82, and 60% yields, respectively.

(6) This nitroolefin was prepared from 3-nitro-2-butanol by dehydration (ref 5), selectively yielding an *E* isomer. The nitroalcohol was obtained in 90% yield by the reaction of nitroethane (0.42 mol) and aqueous acetaldehyde (85% assay, 0.3 mol) in methanolic potassium hydroxide (KOH 19.7 g, MeOH 120 ml) at room temperature for 22 h, followed by acidification with acetic acid and distillation (bp 88–89 ° (9 mm); lit.[18] 92° (10 mm)).

(7) H. O. House, L. J. Czuba, M. Gall, and H. B. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969); G. Stork and P. F. Hudrlik, *J. Am. Chem. Soc.*, **90**, 4462 (1968).

(8) H. E. Baumgarten, P. L. Creger, and C. E. Villars, *J. Am. Chem. Soc.*, **80**, 6609 (1958).

(9) A. M. Islam and R. A. Raphael, *J. Chem. Soc.*, 4086 (1952); P. A. Grieco and C. S. Pogonowski, *J. Org. Chem.*, **39**, 732 (1974); C. H. Heathcock and R. D. Clark, *Tetrahedron Lett.*, 1713 (1974); A. Deboer and R. E. Ellarger, *J. Org. Chem.*, **39**, 77 (1974).

(10) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

(11) J. A. Hartman, *J. Org. Chem.*, **22**, 466 (1957); P. C. Mukharji, P. K. Sen-Gupta, and G. S. Sambamusti, *Tetrahedron*, **25**, 5287 (1969).

(12) G. Stork and M. E. Jung, *J. Am. Chem. Soc.*, **96**, 3683 (1974).

(13) F. Fraise-Jullien and C. Frejaville, *Bull. Soc. Chim. Fr.*, 4449 (1968).

(14) For example, see P. A. Grieco and C. S. Pogonowski, *J. Org. Chem.*, **39**, 732 (1974).

(15) H. Paul and I. Wendel, *Chem. Ber.*, **90**, 1342 (1957).

(16) H. Feuer and R. Miller, *J. Org. Chem.*, **26**, 1348 (1961).

(17) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).

(18) B. M. Vanderbilt and H. B. Haas, *Ind. Eng. Chem.*, **32**, 34 (1940).

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Electronic Spectra of Crystals of Dimolybdenum Tetraformate and the Tetrasulfatodimolybdenum(II) Ion

Sir:

For the quadruply bonded dirhenium and dimolybdenum complexes the lowest energy observed electronic transitions are in the visible region of the spectrum. A computation of one-electron energy states by Dubicki and Martin,[1] who used a SCCC–MO treatment for $Mo_2(O_2CMe)_4$, indicated that the first transition would not be the $\delta \rightarrow \delta^*$ transition. On the other hand more recent calculations by the SCF-Xα scattered wave method by Norman and Kolari[2,3] for $Mo_2Cl_8{}^{4-}$ and for $Mo_2(O_2CH)_4$ have indicated the highest filled orbital is the δ and the lowest unfilled orbital is the δ^*. Polarized absorption spectra on single crystals containing these complexes can provide cogent evidence for assignment of the electronic transitions. The spin-allowed $\delta \rightarrow \delta^*$ transition of M_2X_8 complexes with D_{4h} molecular symmetry is ${}^1A_{1g} \rightarrow {}^1A_{2u}$ and therefore will be dipole allowed with z polarization (z lies along the metal–metal bond). A few such measurements for compounds containing quadruply bonded dirhenium[4,5] and dimolybdenum[6] units suggest that for both $Re_2Cl_6(PEt_3)_2$ and $Re_2Cl_8{}^{2-}$ the band in the visible spectrum may be assigned to the $\delta \rightarrow \delta^*$ transition. For the $Mo_2(O_2CCH_2NH_3{}^+)_4$ unit in $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$,[7] the results show that the lowest energy transition in the visible spectrum *cannot* be so assigned.[6] We wish to report here some new results that help to place the foregoing results in a broader context and thus clarify their significance.

The first question addressed here is whether the results for the $Mo_2(O_2CCH_2NH_3{}^+)_4$ moiety can be considered representative for $Mo_2(O_2CR)_4$ species in general. We have therefore investigated the corresponding low-energy transition in dimolybdenum tetraformate.[8] Polarized spectra for $Mo_2(O_2CH)_4$ at 15 K are presented in Figure 1. The region observed corresponds to that previously studied for $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$.[6] The crystal displayed well-formed 010 faces thus allowing measurement of polarizations parallel to the a and c axes. The Mo–Mo bond (which defines a molecular C_4 axis, the z axis) is aligned 33.4° from the c axis. A z-polarized molecular transition would absorb in both the a and c crystal directions, with $I_c/I_a = 4.3$ while an xy-polarized molecular transition would have $I_c/I_a = 0.36$.

The first absorption is a very narrow band with $\nu_{1/2}$ of 10 cm^{-1} at 21 870 in a and 21 880 cm^{-1} in c polarization. This single band is followed by a pair of bands, each somewhat broader than the first, and then by a group of three bands. Three components can be identified in the fourth and fifth and possibly the sixth group. The spectrum appears to contain three progressions, with a separation of 350 ± 10 cm^{-1} between the successive members of each progression. The low energy bands in each group comprise one progression. The second progression begins with the higher energy band in the pair and includes the intermediate energy members in the higher groups. The third progression includes the high energy members beginning with the third group.

The spectra must be associated with an electronic transition