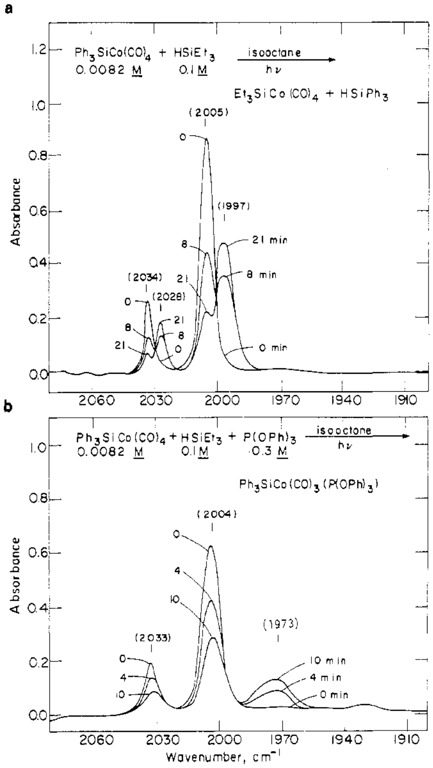

Figure 1. Comparison of the photochemistry of $Ph_3SiCo(CO)_4$ in the presence of $HSiEt_3$ only (a) and $HSiEt_3$ and $P(OPh)_3$ (b). Irradiation of the 25 °C deoxygenated solutions is at 355 nm (±20 nm). Note that the quantum yield for disappearance of $Ph_3SiCo(CO)_4$ is the same in both cases but that silane exchange occurs exclusively in part a, and $P(OPh)_3$ substitution occurs exclusively in part b, consistent with competitive capture of a 16e species by $P(OPh)_3$ or $HSiEt_3$ (eq 5 and 6 in text).

nyl)$SiEt_3$ products are found. Data for the photocatalyzed reactions are given in Table I. The $R_3SiCo(CO)_4$ species lead to extensive pentene isomerization prior to significant extent conversion to (*n*-pentyl)$SiEt_3$. On the order of 10^3 molecules of (*n*-pentyl)$SiEt_3$ have been observed per molecule of $R_3SiCo(CO)_4$ initially added, and the turnover rate for formation of this product is on the order of 25 h^{-1} at the light intensity used to generate data given in Table I. Higher light intensities have yielded observed turnover rates for the reaction of ~250 h^{-1}. Thermal activity of $R_3SiCo(CO)_4$ at 25 °C for (*n*-pentyl)$SiEt_3$ formation is low on the scale of light-induced activity, but significant isomerization is detectable in thermal controls. Table I also shows data that reveal that, when thermal catalytic activity of $Co_2(CO)_8$ is over, catalytic activity can be revived by irradiation. These representative photoactivation data show an additional ~100 turnovers per Co after the catalytic activity for the $Co_2(CO)_8$ is over. While it is tempting to conclude that the same catalyst is generated from irradiation of $Et_3SiCo(CO)_4$ as from $Co_2(CO)_8$ in the dark, we cannot yet unequivocally make this conclusion. We do find that the (*n*-pentyl)$SiEt_3$ is the dominant detectable Si-containing product in both cases. Thus, it would appear that the $Co_2(CO)_8$ activity can be prolonged by irradiation; infrared analysis of the $Co_2(CO)_8$/pentene/$HSiEt_3$ solution when thermal reaction has stopped shows $Et_3SiCo(CO)_4$ to account for >80% of the Co. The photoreaction of $Et_3SiCo(CO)_4$ in pentene to yield (pentenyl)$SiEt_3$ (vide supra) provides a pathway to an active catalyst. The formation of (pentenyl)$SiEt_3$ may occur by first forming $Et_3SiCo(CO)_3$(pentene) followed by insertion to yield (pentyl$SiEt_3$)$Co(CO)_3$ which then rapidly gives β-hydrogen transfer to yield the substitution labile complex (pentenyl$SiEt_3$)$Co(CO)_3H$. This hydride can then lose the (pentenyl)$SiEt_3$ to leave behind the coordinatively unsaturated $HCo(CO)_3$ that is very likely the active catalyst in the $Co_2(CO)_8$ system.[2,5] In addition to determining its role in forming the active catalyst here, further study of this photoreaction is being undertaken to gain insight into the possible mechanism in $Fe(CO)_5$ photocatalyzed reaction of $HSiR_3$/1-pentene that gives substantial amounts of (pentenyl)SiR_3 as a catalysis product.[8,9]

Acknowledgment. We thank the Office of Naval Research for partial support of this research, and M.S.W. acknowledges support as a Dreyfus Teacher-Scholar grant recipient, 1975–1980. C.L.R. was supported during Spring, 1980, by a fellowship with funds generously provided by Eastman Kodak Co.

Registry No. $Ph_3SiCo(CO)_4$, 14095-19-3; $Et_3SiCo(CO)_4$, 14049-72-0; 1-pentene, 109-67-1; pentane, 109-66-0; *trans*-2-pentene, 646-04-8; *cis*-2-pentene, 627-20-3; (*n*-pentyl)$SiEt_3$, 18044-55-8; $Et_3SiCo(CO)_3P(OPh)_3$, 75030-69-2; $Ph_3SiCo(CO)_3P(OPh)_3$, 75030-70-5; $Et_3SiCo(CO)_3$(pentene), 75030-71-6; $Co_2(CO)_8$, 10210-68-1; $Co_4(CO)_{12}$, 17786-31-1; $HSiEt_3$, 617-86-7.

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(8) The isomers have been characterized by GC and mass spectral analyses compared to authentic samples prepared previously: Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345.

(9) (a) Austin, R. G.; Paonessa, R. S.; Giordano, P. J.; Wrighton, M. S. *Adv. Chem. Ser.* **1978**, *No. 168*, 189. (b) Nesmeyanov, A. N.; Friedlina, R. K.; Chukovskaya, E. C.; Petrova, R. G.; Belyavsky, A. B. *Tetrahedron* **1962**, *17*, 61. (c) Friedlina, R. K.; Chukovskaya, E. C.; Tsao, J.; Nesmeyanov, A. N. *Dokl. Akad. Nauk SSSR* **1960**, *132*, 37.

Contribution from Lash Miller Chemistry Laboratory and
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Nickel Vapor/Butadiene Matrix Chemistry

Geoffrey A. Ozin* and William J. Power

Received February 5, 1980

It has recently been demonstrated that nickel atom/olefin matrix cocondensation reactions lead to the formation of a wide range of binary nickel π-olefin complexes of the type Ni(olefin)$_n$, where $n = 1$–3.[1] Each complex displayed a single, intense ultraviolet absorption, which monotonically *blue* shifted with increasing olefin stoichiometry. For a particular stoichiometry, the transition energy was essentially *invariant* to olefin substituent. The insensitivity of this "fingerprint" ultraviolet band, with respect to rather dramatic excursions of the olefinic π and π^* energy levels, pinpointed the electronic transition in question as one involving nickel-localized d → p excitations with only minimal mixing of the Ni (p)/olefin (π^*) orbitals. (This assignment has recently received support from ab initio SCF–HF–LCAO[2] and GVB–CI[3] calculations of $Ni(C_2H_4)_n$.) The optical data established the existence of narrow spectral regions characteristic of olefin stoichiometry, that is, 320–330 nm for Ni(olefin), 280–290 nm for Ni(olefin)$_2$, and 230–250 nm for Ni(olefin)$_3$. Similar correlations were also found for a range of Pd(olefin)$_n$ complexes.[1]

The effect of metal nuclearity on the optical spectra was also investigated in a similar series of experiments under binuclear nickel reaction conditions.[3] In the case of ethylene, $Ni_2(C_2H_4)_{1,2}$ complexes were identified, both displaying bands around 240 and 370–400 nm, quite different from those of $Ni(C_2H_4)_{1,2}$.

With the distinct spectral trends and lack of major substituent effects for numerous mononuclear nickel–olefin complexes, yet considerable sensitivity to metal nuclearity, it is

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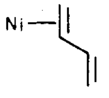
(1) G. A Ozin and W. J. Power, *Inorg. Chem.*, **17**, 2836 (1979).

(2) R. M. Pitzer and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **101**, 7176 (1979).

(3) G. A. Ozin, W. J. Power, W. A. Goddard III, and T. Upton, *J. Am. Chem. Soc.*, **100**, 4750 (1978).

of considerable interest to inquire whether or not optical spectroscopy (in conjunction with vibrational spectroscopy) can be usefully, employed to establish the nature and type of reactive intermediates formed on allowing nickel atoms to interact with 1,3-butadiene under matrix cryogenic conditions. If successful, this optical probe would permit differentiation of a variety of species such as I–VII, all of which are theoretically possible models.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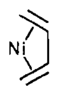
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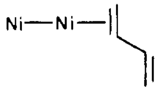
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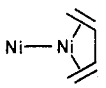
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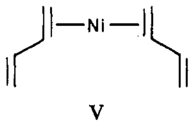
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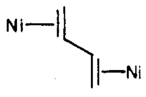
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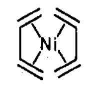
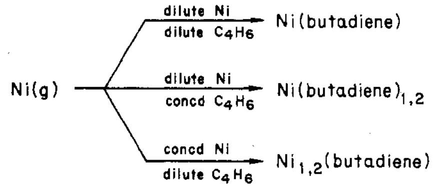

VII

For example, the optical spectrum of I would be predicted to be only slightly perturbed from that of $Ni(C_2H_4)$, while III might be similar to $Ni_2(C_2H_4)$. It would also be anticipated that the optical spectra of II and IV should be quite distinct from those of I and III. Support for the latter proposal originates from some very recent work involving the matrix photochemistry of (η^2-1,3-butadiene)iron tetracarbonyl,[4] which demonstrates that the optical spectrum of the primary photoproduct (η^2-*s-trans*-1,3-butadiene)iron tricarbonyl (400–450 nm) is easily distinguished from that of (η^4-1,3-butadiene)iron tricarbonyl (278 nm).

By employing both ligand and metal concentration experiments in combination with matrix warm-up studies, using methods similar to those described previously,[1,3] it is, in principle, possible to establish nickel atom–butadiene reaction conditions which favor the products shown in the scheme



In this context, recall that Chapman's[5] studies of butadiene/argon matrices (using room-temperature gas mixtures deposited at 20 K) have convincingly demonstrated that the more stable gas-phase rotamer, planar *s-trans*-1,3-butadiene (absorbing at 230 nm), forms almost exclusively on deposition and remains in the *s*-trans conformation during matrix-annealing experiments. In what follows we will briefly describe the optical and IR vibrational spectra obtained for the products of the nickel atom–butadiene reaction.

With the use of mononuclear nickel conditions Ni/Ar ≃ $1/10^4$ and C_4H_6/Ar ≃ 1/20 mixtures, the optical spectra on deposition at 12–15 K showed the presence of *two* distinct products absorbing at 330 and 280 nm with the low-energy absorption always being associated with the species of lowest butadiene stoichiometry, on the basis of the results of ligand dilution and matrix warm-up studies (Figure 1). A possible third mononuclear species D may be obscured by the absorption of free butadiene in argon and pure butadiene matrices, although this suspicion could not be confirmed optically (see later). The spectra show a remarkable resemblence to the optical results of all the aforementioned nickel atom–olefin cocondensation studies,[1] suggesting the mononuclear assignments[6]

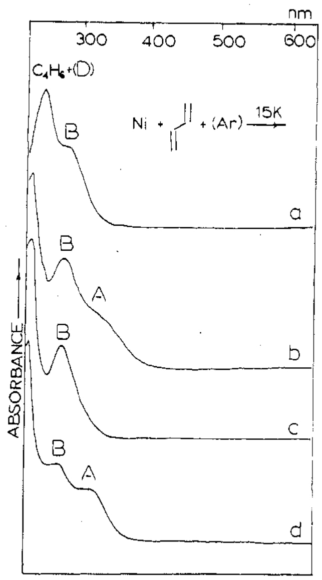
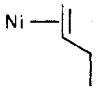
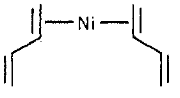


Figure 1. Representative matrix UV–visible absorption spectra observed on depositing nickel atoms under mononuclear conditions (Ni/Ar ≃ $1/10^4$) with a variety of butadiene matrices: (a) pure C_4H_6, (b) C_4H_6/Ar ≃ 1/20, (c) 40 K warm-up of matrix b, and (d) C_4H_6/Ar ≃ 1/50. Note that the absorption energy of free C_4H_6 around 220–230 nm seems to be slightly sensitive to the matrix dilution (see text).


A
330 nm


B
280 nm

Increasing the nickel concentration conditions, Ni/Ar ≃ $1/10^3$, to values which permitted the synthesis of $Ni_2(C_2H_4)_{1,2}$[3] resulted in the initial isolation (C_4H_6/Ar ≃ 1/20) of species B absorbing at 280 nm, in contrast to the nickel–ethylene system which resulted in binuclear complex formation.[7] However, when we annealed these matrices rich in nickel atoms at 35–40 K, a new complex C could be observed to form with absorptions around 420 and 230 nm (the latter observed as a weak shoulder on the absorption of free butadiene). In view of the fact that $Ni_2(C_2H_4)_{1,2}$ also absorb around 370–400 and 240 nm, the new butadiene species C might be assigned to either

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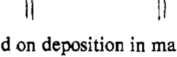
[4] G. Ellerhorst, W. Gerhartz, and F. W. Grevels, *Inorg. Chem.*, **19**, 67 (1980).

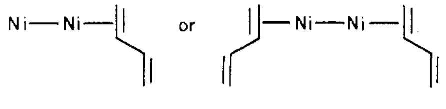
[5] M. E. Squillacote, R. S. Sheridan, O. L. Chapman, and F. A. L. Anet, *J. Am. Chem. Soc.*, **101**, 3657 (1979).

[6] We found that high-temperature depositions, dilute in nickel and butadiene, are not very useful as a possible synthetic route to species such as Ni(η^4-C_4H_6) because nickel-cluster butadiene complexes seem to form preferentially. Thus we are not able to make an unequivocal decision on the existence or nonexistence of Ni(η^4-C_4H_6).

[7] The observation of



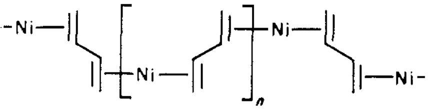
preferentially formed on deposition in matrices relatively rich in nickel [recall that nickel atoms cluster with difficulty under these conditions (M. Moskovits and J. Hulse, *J. Chem. Phys.* **66**, 3988 (1977)), and we only increased the ratio from Ni/Ar ≃ $1/10^4$ to $1/10^3$] is not really surprising when one realizes that *concentrated* butadiene/argon matrices are *better trapping* and *complexing* agents than ethylene/argon matrices under comparable reaction conditions. Hence mononuclear products would tend to be favored in the butadiene system on deposition which could then subsequently agglomerate to higher cluster complexes on matrix annealing at 35–40 K. With the available data, it is difficult to expand any more on this point other than what has already been said in our paper.



C

230 or 420 nm

Collecting together the optical data from a large number of experiments, one can see that the mononuclear and binuclear nickel–butadiene spectra are very similar to those of the nickel–ethylene species, although the conditions for their formation are not strictly comparable. It is interesting to note that a species of type B, bis(*s-trans*-η^2-1,3-butadiene)nickel(0), was recently proposed as an intermediate in the multistep Ni(0)-catalyzed dimerization of 1,3-butadiene.[8] (In view of the ESR data for $Cu(C_2H_2)_2$ and $Cu(C_2H_4)_2$, which favor the D_{2h} planar configuration,[9] it is likely the coordinated double bonds in B also adopt a coplanar geometry.) If such a bonding mode (one double bond corrdinated per butadiene ligand) were generally the case in this system, then the anticipated tris(*s-trans*-η^2-1,3-butadiene)nickel(0) complex D predicted to absorb around 230–250 nm (of relevance to the Ni(0)-catalyzed cyclotrimerization of butadiene to cyclododeca-1,5,9-triene[10]), could well have its absorption masked by the absorption of free butadiene. Furthermore, the proposed polymeric, involatile gray compound formed on reacting nickel vapor with butadiene at 77 K[11] might be understood in terms of the linking together of reactive intermediates of type A, B, or C, to form extended structures possibly of the kind

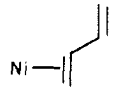


not unlike the structure found for the binuclear complex[12] $(bpy)(\eta^2-C_4H_6)Ni(\eta^2-\mu-C_4H_6)Ni(\eta^2-C_4H_6)(bpy)$.

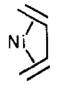
Confirmation of the type of bonding proposed for A, B, and C would be expected to arise from the vibrational spectra of the butadiene complexes, particularly in the $\nu(C{=}C)$ stretching region. Uncomplexed butadiene shows *two* ($\nu(C{=}C)$ modes at 1643 and 1599 cm^{-1},[13] while three η^4 complexes, all of which involve coordination of both double bonds, showed two $\nu(C{=}C)$ modes in the 1500-cm^{-1} region.[14] The species $K_2[(\eta^2-\mu-C_4H_6)(PtCl_3)_2]$[10a] with bridging butadiene (one C=C bond coordinated to each platinum atom) showed $\nu(C{=}C)$ modes at 1521 and 1471 cm^{-1}; $(\eta^4-C_4H_6)Fe(CO)_3$[14b] showed them at 1477 and 1439 cm^{-1}, while $(\eta^4-C_4H_6)_2Fe(CO)$[14c] displayed two bands at 1481 and 1435 cm^{-1}. It can be convincingly argued that a species, such as $Ni(\eta^2-C_4H_6)$, with only one coordinated double bond, should also display two $\nu(C{=}C)$ modes, one around 1500 cm^{-1} for the coordinated moiety and one closer to 1600 cm^{-1}, near those of free butadiene. Strong support for this proposal can be found in the vibrational spectra of the complexes $Pt(PPh_3)_2(\eta^2-C_4H_6)$[15] and $[PtCl_2(\eta^2-C_4H_6)]_2$,[16] which both contain butadiene bound to the platinum as a monolefin complex, the monodentate nature of which is confirmed by the observation of sharp bands at 1605 and 1608 cm^{-1}, respectively, consistent with the expected stretching frequency of an uncoordinated C=C bond.

Deposition of nickel vapor with $C_4H_6/Ar \simeq 1/20$ mixtures under mononuclear nickel conditions at 15 K resulted in the detection of three IR bands at 1496, 1518, and 1532 cm^{-1} in the coordinated $\nu(C{=}C)$ stretching region, which from ligand concentration and variable-temperature annealing studies could be tentatively associated with three distinct species: A, $Ni(C_4H_6)$; B, $Ni(C_4H_6)_2$; and perhaps $Ni(C_4H_6)_3$, respectively. At least two IR bands at 1610 and 1620 cm^{-1} in the nonbonded $\nu(C{=}C)$ stretching region of butadiene always accompanied the aforementioned A,B coordinated $\nu(C{=}C)$ bands. (It should be noted that the IR-active $\nu(C{=}C)$ modes of free butadiene could conceivably obscure some nickel–butadiene complex absorptions.) The IR data therefore provide quite clear evidence in favor of the postulated η^2-butadiene mode of coordination, at least for species A and B. The IR spectra, having supported the bonding proposals for A and B, suggest that the optical spectra are indeed diagnostic indicators for the number and mode of coordination of butadiene ligands to zerovalent nickel. The assignment of the mononuclear complexes could be extended to suggest the stoichiometry of the species absorbing at 230 or 420 nm to be $Ni_2(C_4H_6)_{1,2}$ with the butadiene coordinated in the manner C depicted above, although a bis(η^4-1,3-butadiene)dinickel(0) complex cannot be entirely dismissed as a candidate for C at this time.

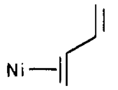
It may at first seem surprising that



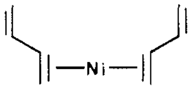
is favored over



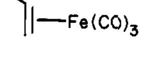
under mononuclear conditions, but this is the conclusion that one is obliged to reach from our experimental data collected over a wide range of matrix reaction conditions. Our experimental results were reproducible, and the deductions based on comparisons with earlier work from our laboratory and from those of others are internally consistent and reasonable. It seems that Ni(0) has no great desire for η^4-coordinated dienes so there is little to be gained by rotating the butadiene ligand to a cisoid geometry. The Chapman–Anet work,[5] which clearly demonstrated the preference for the *s-trans*-butadiene conformational isomer on deposition and warm-up in argon matrices, is particularly pertinent to our Ni/butadiene matrix studies. This conformational preference appears to also hold true for butadiene in its matrix reactions with Ni atoms, to generate our proposed η^2-species



This should not be too surprising in view of (i) the proposed



intermediate in the Ni(0)-catalyzed dimerization of 1,3-butadiene[8], (ii) the requirement of *photochemical excitation* to convert the η^2 reactive intermediate



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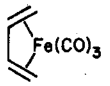
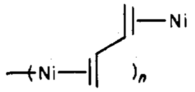
(8) C. R. Graham and L. M. Stevenson, *J. Am. Chem. Soc.*, **99**, 7098 (1977).
(9) P. H. Kasai, D. McLeod, Jr., and T. Watanabe, *J. Am. Chem. Soc.*, **102**, 179 (1980).
(10) G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **2**, 105 (1963).
(11) P. S. Skell, J. J. Havel, D. L. Williams-Smith, and M. J. McGlinchey, *J. Chem. Soc., Chem. Commun.*, 1098 (1972).
(12) G. Wilke, personal communication.
(13) R. K. Harris, *Spectrochim. Acta*, **20**, 1129 (1964).
(14) (a) M. J. Grogan and K. Nakamoto, *Inorg. Chim. Acta*, **1**, 228 (1967). (b) G. Davidson, *ibid.*, **3**, 596 (1969). (c) D. A. Duddell, S. F. A. Kettle, and B. T. Kontnik-Matecka, *Spectrochim. Acta, Part A*, **28A**, 1571 (1972).
(15) A. Sen and J. Halpern, *Inorg. Chem.*, **19**, 1073 (1980).
(16) P. E. Slade and H. B. Jonassen, *J. Am. Chem. Soc.*, **79**, 1277 (1957).

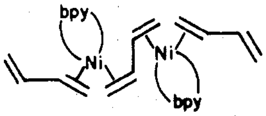
into its η^4 counterpart



(iii) the proposed polymeric nature of the gray product formed from Ni/butadiene at 77 K, which is supposed to contain



repeat units,[8] (iv) the η^2-C_4H_6 bonding mode for the butadiene units in the complex[12]



(v) η^2 bridging in $K_2[(\eta^2\text{-}\mu\text{-}C_4H_6)PtCl_3]_2$,[14a] and (vi) η^2 monodendate bonding for *s-trans*-butadiene in $Pt(PPh_3)_2(\eta^2\text{-}C_4H_6)$[15] and $[PtCl_2(\eta^2\text{-}C_4H_6)]_2$.[16]

In summary, it would appear that the insensitivity of binary nickel–olefin optical spectra to olefin substituents but sensitivity to metal nuclearity may well prove to be a general tool for the characterization of such species, with respect to olefin stoichiometry and mode of olefin coordination. The extension of the work to nickel vapor–polyolefin polymer systems incorporating unsaturated moieties is an obvious next step and one that is already under way in these laboratories.[17]

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Registry No. A, 75112-04-8; B, 45651-77-2.

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(17) C G. Francis, M. Andrews, and G. A. Ozin, work in preparation.

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Synthesis and Characterization of the Organobismuthomolybdates $[(C_6H_5)_3Bi(MoO_4)_2]^{2-}$ and $[(C_6H_5)_3Bi(MoO_4)]_x$

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No heteropolymolybdates containing tetrahedrally coordinated Mo^{VI} are known, a surprising situation since several isopolymolybdates including $Mo_2O_7^{2-}$,[2] $Mo_{10}O_{34}^{8-}$,[3] and α-$Mo_8O_{26}^{4-}$[4] have been shown to contain tetrahedral Mo^{VI}. Due to the basicity and coordinative unsaturation of MoO_4^{2-}, heteropolyanions containing this unit might be expected to display types of reactivity not observed for complexes containing only octahedrally coordinated Mo^{VI}. We have therefore investigated the reactivity of MoO_4^{2-} toward $(C_6H_5)_3BiBr_2$, hoping to obtain not only simple substitution products but also organobismuth(III) reductive elimination products. The isolation of the $[(C_6H_5)_3Bi(MoO_4)_2]^{2-}$ anion and polymeric $[(C_6H_5)_3Bi(MoO_4)]_x$ are reported here. Although attempts to obtain well-characterized reductive elimination products have thus far failed, in the course of such attempts we have discovered a reaction between MoO_4^{2-} and CH_2Cl_2 which results in formation of the $CH_2Mo_4O_{15}H^{3-}$ anion.

Experimental Section

$(C_6H_5)_3BiBr_2$ was prepared according to a literature procedure[5] using CCl_4 as solvent and was recrystallized by slow addition of C_2H_5OH to a saturated $CHCl_3$ solution. $(C_6H_5)_3Bi$ (Eastman Kodak), MoO_3 (Fisher), and 1 M $(n\text{-}C_4H_9)_4NOH$ in CH_3OH (Eastman Kodak) were used without further purification. The solvents CH_2Cl_2, $(C_2H_5)_2O$, $C_6H_5CH_3$, and $(CH_3)_2CO$, all ACS Certified from commercial sources, were not purified. $CHCl_3$ (Fisher, ACS Certified) was distilled over P_2O_5 for ^{17}O NMR measurements only. CH_3CN (Aldrich, 99%) was distilled over P_2O_5 before use as a reaction solvent and was further purified by distillation over CaH_2 before use for conductivity and ^{17}O NMR measurements. Compounds **1** and **2** were enriched to 20 atom % ^{17}O for ^{17}O NMR studies by stirring overnight with enriched water in CH_3CN and $CH_3CN/CHCl_3$ (1:6, v/v), respectively. Enriched compounds were isolated and purified as described below for unenriched samples.

^1H NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer operating at 90 MHz. Proton-decoupled 25.03-MHz ^{13}C NMR spectra and 13.513-MHz ^{17}O NMR spectra were measured at 25 °C by using the pulse FT NMR technique on a Jeol PFT/PS-100 NMR spectrometer interfaced with a Nicolet 1080 data system. ^{17}O chemical shifts were measured relative to pure H_2O (δ 0.0) as described in ref 6b; ^{13}C chemical shifts were measured relative to the $CDCl_3$ solvent (δ 77.0). The conductance of **1** was measured in CH_3CN over a concentration range of 10^{-2}–10^{-4} equiv/L at 25.0 ± 1 °C with use of a Beckman RC-18A conductivity bridge. Elemental analyses and the molecular weight determination were performed by Galbraith Laboratories.

$[(n\text{-}C_4H_9)_4N]_2[(C_6H_5)_3Bi(MoO_4)_2]\cdot 3H_2O$ (1). Method A. A total of 1.30 g of MoO_3 (9.0 mmol) was stirred in 18 mL of 1 M $(n\text{-}C_4H_9)_4NOH$ (18 mmol) in CH_3OH for 6 h and filtered to remove a small amount of unreacted MoO_3. The filtrate was then evaporated under vacuum to a viscous oil containing $[(n\text{-}C_4H_9)_4N]_2MoO_4$. A solution of 2.70 g of $(C_6H_5)_3BiBr_2$ (4.5 mmol) in 20 mL of CH_2Cl_2 was added to this oil. After the resulting solution was stirred for 30 min, an excess of $(C_2H_5)_2O$ was added, and the resulting white precipitate was filtered off and dried in vacuo, 5.15 g (88% yield) of crude product was obtained. Colorless, needle-shaped crystals were grown from this crude product in 88% yield by dissolving it into a solution of 45 mL of CH_3CN in 72 mL of $(C_2H_5)_2O$ and cooling to 0 °C.

Method B. A total of 2.25 mmol of $[(n\text{-}C_4H_9)_4N]_2MoO_4$, prepared as described above for method A in 20 mL of CH_2Cl_2, was added to 1.35 g of $[(C_6H_5)_3Bi(MoO_4)]_x$ (2.25 mmol) and stirred for 30 min. After the solution was filtered, 2.65 g of crude product (91% yield) was isolated by following the procedures employed in method A.

Compound **1** is soluble in organic solvents such as CH_2Cl_2, $CHCl_3$, $(CH_3)_2CO$, CH_3CN, 1,2-$C_2H_4Cl_2$, and C_2H_5OH. Anal. Calcd for $C_{50}H_{93}N_2BiMo_2O_{11}$: C, 46.22; H, 7.21; N, 2.16; Bi, 16.08; Mo, 14.77. Found: C, 46.41; H, 7.35; N, 2.16; Bi, 15.91; Mo, 14.93. ^1H NMR in CD_2Cl_2 displays an *o*-C_6H_5 proton doublet at δ 8.4, a *m*- and *p*-C_6H_5 proton multiplet at δ 7.2–7.7, and an NCH_2 multiplet at δ 3.0–3.4 with relative intensities 5.8:9.2:16.0. ^{13}C NMR (δ, $CDCl_3$, ^1H decoupled): 156.3, 134.6, 130.4 (C_6H_5); 57.8, 23.4, 19.2, 13.2 ($CH_2CH_2CH_2CH_3$).

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