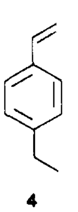
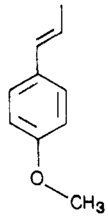
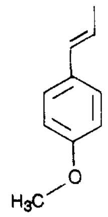

**4**

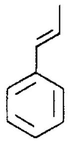

**5s**


**5a**

of only one origin transition for **4** proves that the vinyl group must be in the plane of the ring. This conclusion is further confirmed by the number of spectroscopic origins in the TOFMS of anethole (Figure 2): two $0^0_0$ transitions are observed, one each for the syn **5s** and anti **5a** conformations. Thus, for styrene and other sterically unhindered styrene derivatives, a planar conformation ($\tau = 0°$) in both $S_0$ and $S_1$ obtains.

The TOFMS of $\alpha$-methylstyrene (**3**), shown in Figure 3, is considerably more complex than the simple spectrum obtained for styrene and its sterically unhindered derivatives. In contrast to the intense $0^0_0$ transition observed for styrene, $\alpha$-methylstyrene exhibits a weak origin transition at 35063.7 cm$^{-1}$, blue-shifted with respect to the styrene origin. In addition, a progression in a low-frequency mode ($\approx$69 cm$^{-1}$) is built on this origin. This low-frequency mode is due to the torsional motion about the $C_{ipso}$–$C_\alpha$ bond, described by the coordinate $\tau$ in **2**,[5e,f] since this mode undergoes a significant shift, from 69 to 64 cm$^{-1}$, in the TOFMS of the deuteriated analogue of **3**, namely $PhC(CD_3){=}CD_2$.

Alkyl group substitution generally causes a red-shift in the $S_1 \leftarrow S_0$ transition if the presence of the substituent causes no change in molecular conformation; for example, the $0^0_0$ transition of *trans*-$\beta$-methylstyrene (**6**) is red-shifted by 193.7 cm$^{-1}$ from that of styrene. The blue-shift of the $\alpha$-methylstyrene origin transition with respect to that of styrene by 285 cm$^{-1}$ suggests that **3** is nonplanar in $S_0$. By using the molecular orbital approach developed and employed by Suzuki,[6] we find that $\tau \approx 31°$ for **3** in $S_0$.[7]


**6**

A Franck–Condon intensity analysis of the $S_1 \leftarrow S_0$ torsional progression for **3** results in a displacement of the angle $\tau$ of 30 ± 5° in $S_1$ relative to that in $S_0$.[7] The uncertainty in $\tau$ is due to approximations used for the ground-state potential and the uncertainty in the position of the maxium intensity peak in Figure 3 (8 ± 1). Similar torsional progressions have been observed for 9-phenylanthracene,[8] 9-(2-naphthyl)anthracene,[9] and biphenyl.[10] In these cases of nonrigid aromatics, Franck–Condon analysis has led to the suggestion that a diplacement occurs between $S_0$ and $S_1$ along a torsional coordinate.[8-10] In analogy to biphenyl[10] which is nonplanar in $S_0$ and planar in $S_1$, we suggest that $\alpha$-methylstyrene is twisted by ca. 30° in $S_0$ and is planar in $S_1$.

In conclusion, this work has demonstrated that the vinyl moiety in sterically unhindered styrenes lies in the plane of the aromatic ring in both $S_0$ and $S_1$. Addition of a single methyl group onto the $\alpha$-vinyl carbon of **1** can significantly upset the delicate balance between $\pi$-conjugation and steric destabilization. Nonplanar $S_0$ but planar $S_1$ conformations are the minimum energy geometries for $\alpha$-methylstyrene: $\pi$-conjugation dictates the $S_1$ geometry, whereas steric destabilization dictates the $S_0$ geometry.

**Registry No. 1**, 100-42-5; **3**, 98-83-9; **4**, 3454-07-7; **5**, 104-46-1; **6**, 873-66-5.

---

[6] Suzuki, H. *Electronic Absorption Spectra and Geometry of Organic Molecules*. Academic Press: New York, 1976; Chapter 13.

[7] Complete details of these calculations will appear in the full paper.

[8] Werst, D. W.; Gentry, W. R.; Barbara, P. F. *J. Phys. Chem.* **1985**, *89*, 729.

[9] Werst, D. W.; Brearley, A. M.; Gentry, W. R.; Barbara, P. F. *J. Am. Chem. Soc.* **1987**, *109*, 32.

[10] (a) Im, H.-S.; Bernstein, E. R. *J. Chem. Phys.* **1988**, *88*, 7337. (b) Murakami, J.; Ito, M.; Kaya, K. *J. Chem. Phys.* **1981**, *74*, 6505.

---

## Synthesis and Chemistry of a Dinuclear Iridium Bis-$\mu$-oxo Complex: Observation of Oxygen Transfer and Phosphorus–Carbon Bond Cleavage

William D. McGhee, Thomas Foo, Frederick J. Hollander,
and Robert G. Bergman*

*Department of Chemistry, University of California, and the*
*Materials and Chemical Sciences Division*
*Lawrence Berkeley Laboratory*
*Berkeley, California 94720*

*Received July 25, 1988*

We wish to report the synthesis and chemistry of dinuclear iridium $\mu$-oxo complexes capable of oxygen atom transfer and reaction with C–H bonds.

Treatment of the known,[1] air-stable (trishydroxy)diiridium cation **1** (as its acetate salt **1a**; cf. Scheme I) with lithium diisopropylamide (LDA)[2] in toluene at 25 °C leads to the formation of an extremely air- and moisture-sensitive brick red solid. This material can be isolated in pure form in 30–50% yield. It was identified as the dinuclear bis-$\mu$-oxo complex **2** on the basis of its very simple $^1$H NMR ($\delta$ 1.67 (s) ppm) and $^{13}$C{$^1$H} ($\delta$ 84.6 (s), 11.0 (s) ppm) spectra as well as MS, IR, UV–vis, and elemental analysis properties.[3] Further evidence for the assigned structure was obtained by the rapid reaction of **2** with $H_2O$ to regenerate the starting trihydroxy cation, in this case as the hydroxide salt **1b**.

The bis-$\mu$-oxo complex rapidly transfers oxygen to CO, isocyanates, and phosphines. For example, addition of 4 equiv of CO to a rapidly stirred solution of complex **2** in toluene caused a color change from brick red to yellow-brown after 30 min at ambient temperature, due to the formation of $[Cp^*Ir(\mu\text{-}CO)]_2$ (**3**)[4] (80% NMR yield) and $Cp^*Ir(CO)_2$[5] (5% by NMR) along with the conversion of 2 equiv of CO to $CO_2$.[6] The dinuclear dicarbonyl complex **3** was isolated in 33% yield by crystallization from hexane at −40 °C. Addition of CO to **3** did not lead to the dicarbonyl monomer $Cp^*Ir(CO)_2$; instead, complex **3** was cleanly

---

[1] Nutton, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton, Trans.* **1981**, 1997.

[2] Strong amide bases such as LDA and $(Me_3Si)_2NLi$ have been used extensively to prepare sensitive molecules (e.g., ester enolates and other reactive anions) in organic synthesis (see (a) Fieser, M.; Fieser, L. F. *Reagents for Organic Synthesis*; Wiley-Interscience: New York, Vol. 11, p 296 and references cited therein). Sharp and his co-workers have utilized this method in the synthesis of $\mu$-oxo complexes in the rhodium series related to the ones described here ((b) Sharp, P. R.; Flynn, J. R. *Inorg. Chem.* **1987**, *26*, 3231), and we have employed it in an organometallic ring closure leading to oxa- and azametallacycles ((c) Klein, D. P.; Hayes, J. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3704).

[3] Complexes **2**, **3**, **5a**,**b**, **6a**–**c**, **7a**,**b**, **8a** have been characterized by $^1$H NMR, $^{13}$C{$^1$H} NMR, $^{31}$P{$^1$H} NMR (where applicable), IR, and mass spectrometry and elemental analysis. Complex **4** has been characterized by $^1$H NMR, IR, and mass spectrometry. Details are provided as Supplementary Material.

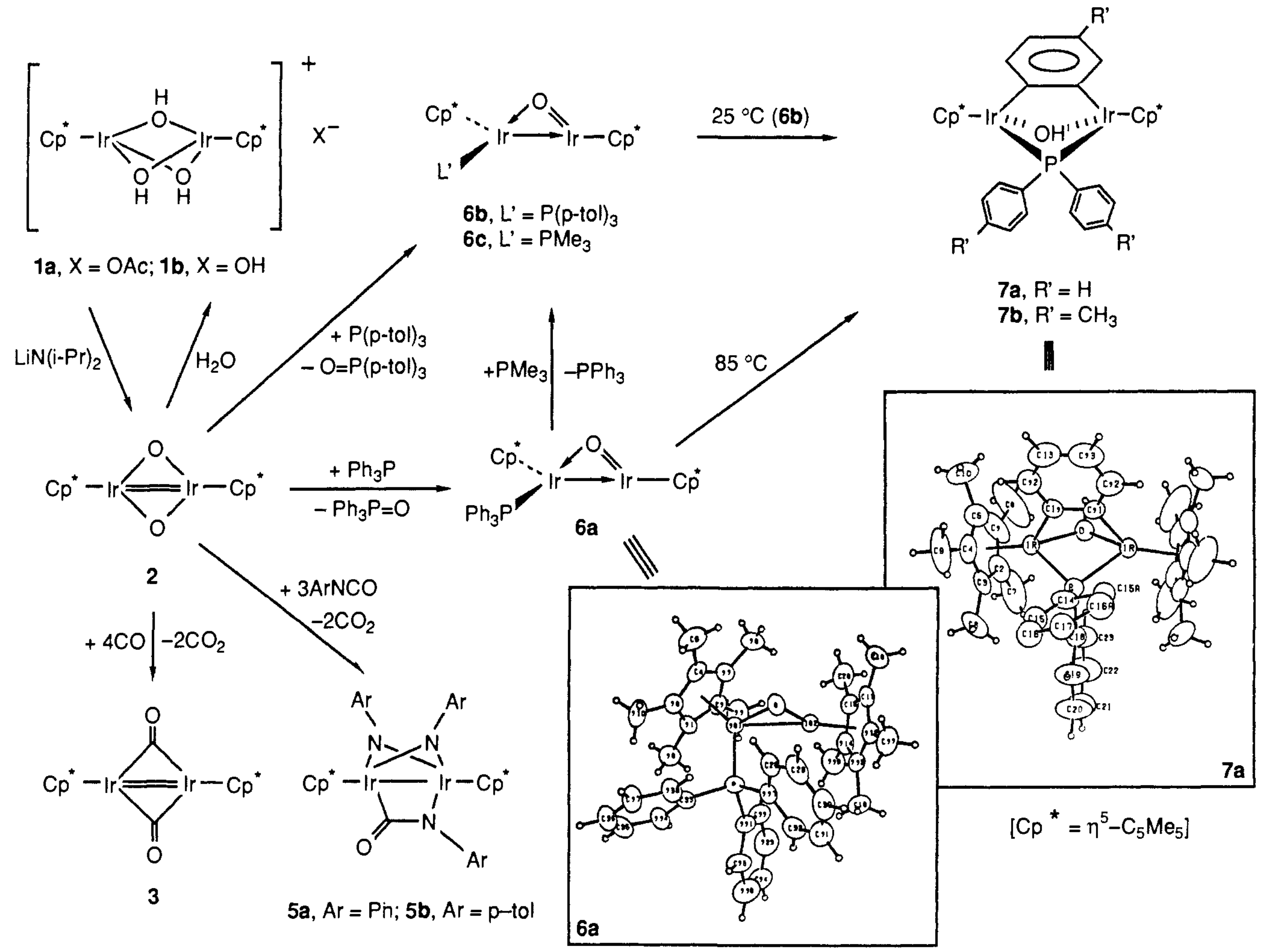
[4] Chetcuti, P. A.; Hawthorne, F. M. *J. Am. Chem. Soc.* **1987**, *109*, 942. Although the dicarbonyl dimer **3** has been previously reported, no details of its synthesis or spectral data beyond a $^1$H NMR spectrum have appeared. Consequently, its full spectroscopic and analytical characterization is provided in the Supplementary Material. A more efficient synthesis of complex **3** has been reported: Graham, W. A. G.; Heinekey, D. H., private communication.

[5] Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

[6] The conversion of CO to $CO_2$ by a bridging transition-metal oxo complex has appeared in only one other account: Herrmann, W. A.; Serrano, R.; Schafer, A.; Kusthardt, U. *J. Organomet. Chem.* **1984**, *272*, 55.

0002-7863/88/1510-8543$01.50/0

**Scheme I**



converted to the dinuclear tricarbonyl complex $Cp^*_2Ir_2(CO)_3$ (**4**,[3] not shown in Scheme I), which is stable toward further addition of CO. The source of the trace amounts of $Cp^*Ir(CO)_2$ has yet to be determined. Addition of arylisocyanates ArNCO (*a*: Ar = Ph; *b*: Ar = *p*-tol)[7,8] to a toluene solution of complex **2** gives complexes formulated as **5** on the basis of spectral and analytical data.[3] The formation of these products may involve the reaction of the bis-μ-oxo complex **2** with 2 equiv of isocyanate to produce the bis-μ-imido species $Cp^*_2Ir_2(\mu\text{-}NAr)_2$, which is subsequently trapped by a third equivalent of isocyanate. The appearance of a bridging isocyanate is rare, although examples of $\eta^2$-isocyanates have been reported for mononuclear systems.[9] Recently, an isocyanate has been reported to bridge three metal centers.[10]

The addition of 2 equiv of phosphine ($PPh_3$ or P(*p*-tol)$_3$) to compound **2** in toluene immediately caused a color change in the solution from red to dark olive green. Integration of the $^1H$ NMR spectrum demonstrated that **2** had been converted to complexes **6** (100% yield by NMR, 74% isolated for **6a**; 48% isolated for **6b**) and 1 equiv of phosphine oxide. The $^1H$ and $^{13}C\{^1H\}$ NMR spectra of complexes **6a** and **6b** show two inequivalent Cp* resonances. For compound **6a**, doublets corresponding to the Cp* ligand residing on the same iridium center as the coordinated phosphine appear at δ 1.87 ppm ($J_{HP}$ = 1.7 Hz) in the $^1H$ NMR spectrum and at δ 92.0 ppm ($J_{CP}$ = 4.4 Hz) for the ring carbons in the $^{13}C\{^1H\}$ NMR spectrum. Singlets appearing at δ 1.28 ppm in the $^1H$ NMR spectrum and at δ 81.4 ppm in the $^{13}C\{^1H\}$ spectrum correspond to the other Cp* ligand. The mass spectrum shows a clean parent peak at $m/e$ = 932.

Crystals of **6a** suitable for single-crystal X-ray diffraction were obtained by slow cooling of a pentane solution to −40 °C. An ORTEP diagram of the compound is included in Scheme I, and details of the structure determination are provided as Supplementary Material.[11] The most striking aspect of the structure is the large difference between the two Ir–O distances (2.035 (4) Å vs 1.858 (4) Å), suggesting a difference in the bond order of the two Ir–O bonds. This may be due to the presence of one single and one double Ir–O bond, as illustrated in the scheme, or it may be enforced by the bulky phosphine ligand which is attached to the metal center having the longer Ir–O linkage. An Ir–Ir bond (2.617 (1) Å) is assumed to maintain a formal 18-electron count about each Ir center. To our knowledge, unsymmetrically bridged μ-oxo complexes for iridium have previously been unknown, and those for other metals are rare.[12]

Complexes **6** give up their oxygen atom much less readily than does **2**. Thus, treatment of **6a** with additional triphenylphosphine, or with more nucleophilic phosphines such as $PMe_3$, does not result in the formation of additional phosphine oxide. Instead, substitution occurs, **6a** undergoing conversion smoothly to **6c** with a half-life of about 10 h at 45 °C. The mechanism of this substitution is not known; possibilities are a dissociative process to

---

(7) For a review on transition-metal imido complexes, see: Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

(8) For a review on the use of isocyanates in transition-metal chemistry, see: Cenini, S.; LaMonica, G. *Inorg. Chim. Acta* **1976**, *18*, 279.

(9) Kolomnikov, I. S.; Koreshkov, Y. D.; Loobeeva, T. S.; Volpin, M. E. *Izv. Akad. Nauk. SSSR Ser. Khim.* **1972**, 1181.

(10) Bhaduri, S.; Khwaja, H.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1988**, 194.

(11) The structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques. Crystal data for **6a** at 25 °C: space group $P2_1/n$; $a$ = 10.7423 (13) Å, $b$ = 26.2904 (26) Å, $c$ = 14.1106 (16) Å; $\beta$ = 92.707 (8)°; $V$ = 3980.7 (13) Å$^3$; $Z$ = 4; $d_c$ = 1.56 g cm$^{-3}$; $\mu_{calcd}$ = 67.2 cm$^{-1}$; $R$ = 2.52%, wR = 2.96%, GOF = 1.56, $n_{var}$ = 404, $n_{obsd}$ = 3796.

(12) Herrmann, W. A. *J. Organomet. Chem.* **1986**, *300*, 111.

generate the intriguing intermediate $Cp^*{}_2Ir_2(\mu\text{-}O)$ or bimolecular pathways in which the incoming phosphine adds either to the metal center to which $PPh_3$ is bound or to the remote center to give an intermediate or transition state $Cp^*(L)Ir(\mu\text{-}O)Ir(L')Cp^*$.

The most dramatic transformation of the phosphine $\mu$-oxo complexes **6a**,**b** occurs upon heating them in benzene or toluene solution without added reagents. This leads to new materials (**7a** and **7b**) which have been formed by deep-seated rearrangement. In the case of **6a**, the product is formed after 45 min at 85 °C in 85% isolated yield; **6b** is converted more readily, forming a 31% isolated yield in 2 days at 25 °C (both are isolated as golden yellow solids). The appearance of strong IR bands (3507 $cm^{-1}$ for **7a**; 3525 $cm^{-1}$ for **7b**) indicated the presence of an O–H group in each molecule. Further evidence for an O–H group includes a high field $^1H$ NMR resonance ($\delta$ −3.43 ppm in $C_6D_6$ for **7a**: d, $J_{HP}$ = 13.8 Hz; −3.48 for **7b**: d, $J_{HP}$ = 13.5 Hz), which disappears upon addition of $D_2O$. In combination with $^1H$ and $^{13}C$ NMR spectra, these data suggested the structure shown in Scheme I for the rearranged products. In support of this formulation, complex **7a** has been degraded with HCl in toluene-$d_8$ to give benzene (identified by $^1H$ NMR and GC/MS) and $Cp^*Ir(HPPh_2)Cl_2$ (**8a**,[3] identified by $^1H$ and $^{31}P$ NMR) as the major identifiable products. Degradation of the analogous complex **7b** in $C_6D_6$ similarly yields toluene (identified by $^1H$ NMR and GC/MS) and $Cp^*Ir(HPTol_2)Cl_2$ (**8b**, identified by $^1H$ [$\delta$ 1.31 (d, $J$ = 2.3, Cp*)] and $^{31}P$ NMR [$\delta$ −12.3 (d, $J$ = 407.5)]). The structure of **7a** has been confirmed by X-ray diffraction; an ORTEP diagram is included in Scheme I, and details are provided as Supplementary Material.[13]

In recent years much attention has been directed toward the possible role of reactive transition-metal oxo complexes as oxidizing and oxygen-atom-transfer agents.[14] However, there have been very few reports of isolable oxo complexes of the noble metals[2b,15] (especially those noted for undergoing rapid C–H insertion reactions) because the M–O bond is generally stabilized by highly oxidized and electron-deficient metal centers.[14] Although late transition metals have been shown to cleave P-aryl bonds to form benzyne complexes,[16,17] the transfer of the H atom from a C–H bond to an oxygen atom receptor in the conversion of **6** to **7** is, to our knowledge, so far unique to this system. It is our hope that the successful construction of additional low-valent, electron-rich transition-metal oxo species, which exhibit enhanced reactivity at both the metal and oxygen sites, will assist in the development of materials useful in the oxygenation of traditionally inert organic molecules.[18]

**Acknowledgment.** We are grateful for financial support of this work from the National Science Foundation (CHE-8722801). T.F. acknowledges a fellowship from the NSF. We are also grateful to the Johnson-Matthey Corp. for a generous loan of iridium chloride and to Prof. Paul R. Sharp (University of Missouri, Columbia) for helpful discussions and for disclosing results prior to publication.

**Supplementary Material Available:** Spectroscopic and analytical data for complexes **2**, **3**, **4**, **5a**,**b**, **6a**,**c**, **7a**,**b**, and **8a**, and details of the structure determination of complexes **6a** and **7a** including experimental description, ORTEP drawings showing full atomic numbering scheme, crystal and data collection parameters, anisotropic thermal parameters (B's), positional parameters and their estimated standard deviations, and intramolecular distances and angles (46 pages); tables of calculated and observed structure factors for **6a** and **7a** (47 pages). Ordering information is given on any current masthead page.

---

[13] The structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques. Crystal data for **7a** at 25 °C: space group *Pcbm*; $a$ = 8.7305 (9) Å, $b$ = 20.8495 (13) Å, $c$ = 21.9477 (19) Å, $\alpha = \beta = \gamma = 90.0°$; $V$ = 3995.1 (10) $Å^3$; $Z$ = 4; $d_c$ = 1.70 g $cm^{-0}$; $\mu_{calcd}$ = 67.0 $cm^{-1}$; $R$ = 2.26%, wR = 3.06%, GOF = 1.54, $n_{var}$ = 236, $n_{obsd}$ = 2026.

[14] For a review on metal-centered oxygen-atom-transfer reactions, see: Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

[15] (a) Carty, P.; Walker, A.; Mathew, M.; Palenik, G. J. *J. Chem. Soc., Chem. Commun.* **1969**, 1374. (b) Brownlee, G. S.; Carty, P.; Cash, D. N.; Walker, A. *Inorg. Chem.* **1975**, *14*, 323. (c) Cheng, P.-T.; Nyburg, S. C. *Inorg. Chem.* **1975**, *14*, 327.

[16] Brown, S. C.; Evans, J.; Smart, L. E. *J. Chem. Soc., Chem. Commun.* **1980**, 1021.

[17] For a review on transition-metal-mediated phosphorus–carbon bond cleavage reactions, see: Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171.

[18] For reviews of C–H activation, see: (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Riedel Publishing Co.; Dordrecht, 1984. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

---

## Tubular Silicate-Layered Silicate Intercalation Compounds: A New Family of Pillared Clays

Ivy D. Johnson, Todd A. Werpy, and Thomas J. Pinnavaia*

*Department of Chemistry and*
*Center for Fundamental Materials Research*
*Michigan State University*
*East Lansing, Michigan 48824*

*Received May 22, 1988*

Metal oxide pillared clays[1-9] are among the most promising microporous materials to be developed since the advent of synthetic zeolites more than four decades ago. Interest in these materials is stimulated in part by their properties as heterogeneous catalysts, especially for the shape-selective cracking of petroleum to high-energy fuels.[10-12] These materials normally are prepared by intercalative ion exchange of smectite clays with polyoxocations, followed by thermal conversion of the intercalated ion to metal oxide aggregates of molecular dimension.

Several workers have recognized the possibility of directly intercalating metal oxide sol particles into clay galleries.[13-16] However, the formation from sols of pillared clay derivatives with *uniform* gallery heights presupposes the existence of pillaring particles of rigorously uniform size and shape. Although nonaggregated sols in the submicron range are routinely available, those with sizes approaching molecular dimension (<50 Å) are difficult to produce in monodispersed form.

We have found that a sol containing the tubular metal oxide imogolite[17-20] can be directly intercalated as a regular monolayer in the galleries of smectite clays. These novel intercalates, schematically shown in Figure 1, are regular tubular silicate-layered silicate (TSLS) nanocomposites that constitute a new

---

[1] Vaughan, D. E. W.; Lussier, R. J. *Preprints 5th International Conference on Zeolites*; Naples, Italy, June 2–6, 1980.

[2] Pinnavaia, T. J. *Science* **1983**, *220*, 365.

[3] Lahav, N.; Shani, V.; Shabtai, J. *Clays Clay Miner.* **1978**, *26*, 107.

[4] Loeppert, R. H., Jr.; Mortland, M. M.; Pinnavaia, T. J. *Clays Clay Miner.* **1979**, *27*, 201.

[5] Yamanaka, S.; Brindley, G. W. *Clays Clay Miner.* **1979**, *27*, 119.

[6] Sterte, J.; Otterstedt, J. *Applied Cat.* **1988**, *38*, 131.

[7] Adams, J. M. *Applied Clay Science* **1987**, *2*, 309.

[8] Tilak, D.; Tennkoon, B.; Jones, W.; Thomas, J. M. *J. Chem. Soc., Faraday Trans.* **1986**, *82*, 3081.

[9] Barrer, R. M. Zeolites and Clay Minerals as Sorbents and Molecular Sieves. Academic Press: New York, 1978.

[10] Shabtai, J.; Lazar, R.; Oblad, A. G. *Stud. Surf. Sci. Catal.* **1981**, *7*, 828.

[11] Occelli, M. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 253.

[12] Lussier, R. J.; Magee, J. S.; Vaughan, D. E. W. *Preprints 7th Canadian Symposium on Catalysis*; Edmonton, Alberta, Canada, October 19–22, 1980.

[13] Occelli, M. L. *Proceedings of the International Clay Conference*; Denver, CO, July 28–August 2, 1985, 319.

[14] Yamanaka, S.; Nishihana, T.; Okumera, F.; Hattori, M. *Abstracts of Papers*, 24th Meeting of the Clay Mineral Society 1987.

[15] Moini, A.; Pinnavaia, T. J. *Solid State Ionics* **1988**, *26*, 119.

[16] Occelli, M. L. *J. Mol. Catal.* **1986**, *35*, 377.

[17] Yoshinaga, N.; Aomine, S. *Soil Plant Nutr.* **1962**, *8*, 6.

[18] Farmer, V. C.; Fraser, A. R. *J. Chem. Soc., Chem. Commun.* **1977**, *13*, 462.

[19] Farmer, V. C.; Adams, M. J.; Fraser, A. R.; Palmieri, F. *Clay Miner.* **1983**, *18*, 459.

[20] van der Gaast, S. J.; Wada, K.; Wada, S.-I.; Kukuto, Y. *Clays Clay Miner.* **1985**, *33*, 237.

0002-7863/88/1510-8545$01.50/0