(4) Å),[8] the intramolecular $Au\cdots Au$ distance in $Au_2(dmb)(CN)_2$ (3.536 Å),[9] the van der Waals contacts (3.4 Å)[11] and the typical $r(Au_2)$ values (2.76–3.10 Å) for Au(I) dimers[12–16] and aggregates,[17] and the interatomic distance in Au metal (2.884 Å).[18] The value of the Au_3 angle is 163.66 (4)° and is similar to that reported for the polymeric 1D $AuTl(MTP)_2$ (MTP = $Ph_2P(CH_2)S$),[19] where the Au–Tl–Au′ and Tl–Au–Tl′ angles are 162.7 (1) and 162.9 (1)°, respectively. The solid $Au_2(tmb)Cl_2$ appears to be the first example of a 1D Au(I) material without halogen-bridging units.

The solid-state UV–visible spectra exhibit an absorption at 292 nm for $Au_2(tmb)Cl_2$ in KBr pellets.[20] In solution, this band is also observed $\lambda_{max} = 272$ nm, suggesting that this low-energy band does not arise from $Au\cdots Au$ interactions; a metal-centered d → p assignment is preferred.[20b] The solid-state luminescence spectrum (Figure 2) exhibits a maximum at 417 nm ($\tau_e = 0.70 \pm 0.03$ μs).[21] This excited-state energy (~2.9 eV) correlates well with those reported for solid $K[Au(CN)_2]$ (~3.1 eV at 78 K),[10b] solid $Au_2(dmb)(CN)_2$ (~2.8 eV at 293 K),[9] and some Au_2 compounds in solution.[22] The long lifetime and large separation between absorption and emission peaks (~10 400 cm^{-1}) indicate that the luminescence is phosphorescence.

The solid-state vibrational spectra were also obtained in the 30–450-cm^{-1} range (ν(Au–Cl) = 352 (IR), 359 cm^{-1} (R); ν(Au–C) = 417 (IR), 390 cm^{-1} (R)). The intense Raman active intermolecular $\nu(Au\cdots Au)$ mode is found in the lattice vibration region at 50 cm^{-1}.[23] The associated force constant, $F(Au\cdots Au)$, is 0.15 mdyn $Å^{-1}$. From an empirical equation relating $r(M\cdots M)$ and $F(M\cdots M)$ for the 5d elements ($r(M\cdots M) = 2.01 + 1.31 \times \exp(-F/2.36)$),[26] a 3.24-Å value for $r(Au\cdots Au)$ was obtained, which compares reasonably well with the observed $r(Au\cdots Au)$ of 3.31 Å (~2% difference). The only other reported $\nu(Au_2)$ value for nonbonded Au_2 compounds was located at 64 cm^{-1} [24] for $Au_2(ylid)_2$ (ylid = $Ph_2P(CH_2)_2^-$),[25] for which the intramolecular $Au\cdots Au$ separation is ~3.0 Å.[25] Other low frequencies have been observed in other weakly interacting M_2 complexes; $\nu(Rh)_2 = 60$ cm^{-1} [27a] and $r(Rh_2)$ = 3.193 Å[27b] for $[Rh(CNPh)_4]_2^{2+}$.

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Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, and data collection parameters for $Au_2(tmb)Cl_2$ (4 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(20) (a) The UV–visible spectra in CH_3CN solutions exhibit three maxima at 196 (63 200), 232 (19 000) and 274 nm (5110 M^{-1} cm^{-1}) and a shoulder at 216 nm (~15 000 M^{-1} cm^{-1}). The absorption spectrum of solid $Au_2(tmb)Cl_2$ is the same in NaCl, KBr, and CsI pellets. (b) This assignment is consistent with that for the $M(PPh_3)_3$ complexes (M = Pd(0), Pt(0)): Caspar, J. V. *J. Am. Chem. Soc.* **1985**, *107*, 6718. Recent SCF–Xα–SW molecular orbital calculations have suggested that substantial mixing of the d_{z^2} orbital with the s orbital occurs during the formation of the $d\sigma^*$ molecular orbital in the $[Au_2(H_2PCH_2PH_2)_2]^{2+}$ compound.[22] Although there is no experimental evidence for d_{z^2}–s–p_z orbital mixing in the mononuclear d^{10} complexes, the possibility of such a situation occurring remains. In solid $Au_2(tmb)Cl_2$, the intermolecular $Au\cdots Au$ distances are too large (~3.3 Å) to observe significant Au_n interactions forming bonding and antibonding molecular orbitals. The electronic absorption spectra in the solid state are not so different from those in solution. The metal-centered d → p assignment is preferred.

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Synthesis and Photochemical Reactions of a Layered Manganese Carbonyl–Zirconium Hydrogen Phosphate Compound

A large number of organometallic guest molecules have been intercalated into inorganic layered and zeolitic host lattices.[1,3] In the case of layered hosts, the layers separate to accommodate the guest, giving a material with alternating organometallic and inorganic layers. The most common reactions used to promote this intercalation are redox and ion exchange processes.[1,2] A Brønsted acid/base reaction has also been used to promote intercalation of organometallics, but has been restricted to substituted ferrocenes.[3] This communication reports the intercalation of an amine-substituted organometallic carbonyl complex into the acidic layered host α-$Zr(HPO_4)_2 \cdot H_2O$, ZrP. Photolysis of this intercalated metal carbonyl leads to a surface-supported organometallic complex.

The dimeric manganese tricarbonyl complex $[(CO)_3Mn(\eta^5\text{-}C_5H_3(CH_3)CH_2-)]_2NH$, Mn_2-NH, was prepared by first for-

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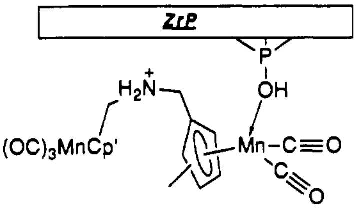
mylating Cp′Mn(CO)$_3$ to give a mixture of α- and β-isomers of [η^5-$C_5H_3(CH_3)(HC{=}O)$]Mn(CO)$_3$.[4] The formyl complex is converted into the secondary amine dimer by treatment with $NaBH_3(CN)$ and NH_4OAc in methanol;[5] yield = 45%.[6]

ZrP is a layered material with phosphinol groups (≡P—OH) covering the surfaces of the host lamella.[7] The Mn$_2$-NH intercalation compound is prepared by treating a powdered sample of ZrP with a methanol solution of Mn$_2$-NH (3 equiv based on zirconium) at 55 °C for 3 days. The intercalated product, $[(Mn_2\text{-}NH)H^+]_{0.3}Zr(HPO_4)_{1.7}(PO_4^-)_{0.3}\cdot 0.7H_2O$, Mn$_2$-NH·ZrP, has an interlayer separation of 20.2 Å,[8] compared to 7.56 Å for ZrP.[7c] This observed interlayer separation is consistent with a bilayered arrangement of guest molecules between host monolayers, as is typically observed for amine intercalation compounds.[2,7b] Thermogravimetric analysis of Mn$_2$-NH·ZrP under vacuum shows loss of H_2O (3.0% weight loss) between 60 and 100 °C. Between 150 and 350 °C, a two-step weight loss is observed (18 and 10%), the sum of which equals that expected for complete loss of Mn$_2$-NH. The FT-IR and ^{13}C CP MAS NMR spectra of Mn$_2$-NH·ZrP and Mn$_2$-NH·HCl are very similar.[6,9] The ^{13}C resonance for the CO ligands in Mn$_2$-NH·ZrP is significantly more narrow than that observed for Mn$_2$-NH·HCl,[10] suggesting that additional motional averaging of the Mn(CO)$_3$ unit may occur in the intercalation compound, possibly due to faster axial rotation.

Photolysis of Mn$_2$-NH·ZrP using a Pyrex-filtered 550-W medium-pressure Hg lamp leads to a steady decrease in the $\nu_{C\equiv O}$ absorptions in the IR spectrum (ca. 50% decrease after 150 min of irradiation). New bands at 2176, 2121, and 1834 cm^{-1} grow in during the early stages of the photolysis, but ultimately disappear on extensive irradiation (500 min). It is well-known that Cp′Mn(CO)$_3$ will lose a CO ligand when irradiated;[11] photolysis in ethanol gives Cp′Mn(CO)$_2$(HOEt), which has $\nu_{C\equiv O}$ bands at 1918 and 1842 cm^{-1}.[11b] We assign the band at 1834 cm^{-1} to a phosphinol-bound manganese dicarbonyl complex, A (for clarity, only the ZrP phosphinol coordinated to Mn is shown); the band corresponding to the 1918-cm^{-1} stretch should fall under one of the Mn$_2$-NH·ZrP bands and should not be observed. The final product of this photolysis, B, shows no $\nu_{C\equiv O}$ absorptions in the IR spectrum, but still shows the expected absorptions for the cyclopentadienyl ligand. Powder X-ray diffraction patterns recorded throughout the photolysis show only peaks due to Mn$_2$-NH·ZrP, which ultimately disappear on formation of the amorphous product B. B is a paramagnetic material giving a broad resonance in the ^{13}C CP MAS NMR centered at 139 ppm. The ESR spectrum of B is a six-line pattern with an isotropic coupling constant $a_{^{55}Mn}$ of 54 G and a *g* value of 2.013, which is very similar to that observed for low-spin cyclopentadienyl Mn^{II} compounds.[12] IR and ESR spectroscopies suggest that B is a phosphinol-bound CpMn^{II} complex. To the best of our knowledge, this is the first example of metal carbonyl photochemistry being carried out inside a layered intercalation compound.



A

The phosphinol intermediate A can also be thermally converted to B. If Mn$_2$-NH·ZrP is photolyzed for 75 min, a sample is obtained in which the 1834-cm^{-1} band of A has an integrated intensity 20% that of the 1925-cm^{-1} band of Mn$_2$-NH·ZrP. After the sample is allowed to stand overnight at room temperature, the 1834-cm^{-1} band decreases by a factor of 10 while the parent bands are essentially unchanged, relative to an internal reference.[13] This suggests that the reaction is not reversing to the starting complex but proceeding to a CO-free compound, presumably B. This thermal reaction, as well as the photochemical conversion of A to B, makes it impossible for us to obtain samples where A represents more than 5–10% of the material.

The higher energy absorptions at 2176 and 2121 cm^{-1} come from dissociated CO trapped inside the layered material. CO in zeolite Y, a good model for CO trapped in these intercalated materials, shows two broad absorptions centered at 2170 and 2120 cm^{-1}.[14] One possibility for the 2176-cm^{-1} stretch was an intercalated manganese–N$_2$ complex ($\nu_{N\equiv N}$ for CpMn(CO)$_2$N$_2$ = 2165 cm^{-1}).[11a,15] If Mn$_2$-NH·ZrP is prepared and photolyzed under Ar, bands at 2176 and 2121 cm^{-1} are still observed, demonstrating that the 2176-cm^{-1} band is not due to an N$_2$ complex. Mn$_2$-NH·ZrP can be dehydrated by heating the sample to 75 °C under vacuum for 2 h. Photolysis of dehydrated Mn$_2$-NH·ZrP gives a compound with an 1834-cm^{-1} band (assigned to A), but the bands attributed to trapped CO are not observed. On dehydration passages are opened for the water to escape; these channels may remain open, permitting the liberated CO to diffuse out. The photochemistry of the dehydrated material also demonstrates that the interlayer water does not participate in this reaction.

Amine substitution into the periphery of organometallic complexes is an effective way to prepare layered organometallic intercalation compounds. These layered materials promise to be an excellent way to study the thermal and photochemical reactions of organometallic complexes with inorganic surfaces.

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Supplementary Material Available: FT IR spectra of Mn$_2$-NH·ZrP after 0, 150, and 500 min of photolysis and ^{13}C CP MAS NMR spectra of Mn$_2$-NH·ZrP and Mn$_2$-NH·HCl (2 pages). Ordering information is given on any current masthead page.

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(10) Full width at half-height for Mn$_2$-NH·ZrP = 130 Hz and for Mn$_2$-NH·HCl = 770 Hz. The spectra were recorded with a JEOL 270-MHz CPMAS NMR spectrometer (67.9 MHz for ^{13}C) and are available in the supplementary material.

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