Table I. Distribution of Tritium in Representative Compounds Labeled by HNaY Zeolite Catalysis[a, b]

compound	time, h	^{3}H incorp, %	^{3}H incorp/site, %			
			ortho	meta	para	other
$PhCH_3$	1.5	12.5	28.7	<1	42.5	<1 (alkyl)
$PhCH_3$	7	100	29.5	3.3	34.4	<1 (alkyl)
Ph-*n*-C_7H_{15}	48	22	26.5	2.2	42.5	<1 (alkyl)
$PhCH(CH_3)_2$	15	43	7.5	<1	16.2	*c*
$PhCH(CH_3)CH_2CH_3$	16	74	15.9	2.6	30.9	*d*
PhBr	24[e]	30	13.2	<1	73.6	
$PhNH_2$	74	11	39.5	<1	21.1	
PhOH	73	93	30.2	7.0	25.5	
$PhOCH_3$	2	65	32.2	<1	35.6	<1 (alkyl)
furan	74	62				50 (α), <1 (β)
thiophene	74	100				28 (α), 22 (β)
naphthalene	20	27				22 (α), 2.8 (β)
$PhSi(CH_3)_2H$	40	7.6	o,p33	CH_3 <1	SiH <1	

[a] Zeolite prepared from Linde SK40 exchange NH_4NO_3 to 3% residual Na and activation to 470 °C. [b] ^{3}H NMR assignments as per literature where available. Other chemical shifts assigned as follows (ppm relative to Me_4Si of pure compound derived as in ref 4). *n*-Heptylbenzene: *o*, 7.04; *m*, 7.14; *p*, 7.06. Isopropylbenzene: *o*, 7.08; *m*, 7.14; *p*, 7.03; CH, 2.55; CH_3, 1.09. *sec*-Butylbenzene: *o*, 7.07; *m*, 7.15; *p*, 7.04; CH, 2.40; CH_2, 1.46, 1.49; β-CH_3, 1.12; γ-CH_3, 0.73. Aniline: *o*, 6.35; *m*, 7.05; *p*, 6.69. Phenol: *o*, 7.36; *m*, 7.56; *p*, 7.30. Anisole: *o*, 6.77; *p*, 6.82. Thiophene: α, 7.00; β, 6.88. [c] Alkyltritium (%): CH, <1; CH_3, 11.5. [d] Alkyltritium (%): CH, <1; CH_2, 6.7; β-CH_3, 6.2; γ-CH_3, <1. [e] Reaction temperature 195 °C for PhBr.

induced exchange to electrophilic substitution have been reported previously.[6]

No labeling was observed within the alkyl substituent of the straight-chain alkyl aromatics. In branched alkyl aromatics, alkyl exchange was confined to the β-carbon atoms of molecules branched at the α carbon. Such a substitution pattern is expected where exchange involves hydride transfer between the reactant molecule and an α-carbonium ion, as proposed elsewhere.[7,8] Incorporation of tritium into the carbonium ion may take place by deprotonation to an olefinic intermediate and reprotonation.[8,9]

Attempts to label *n*-alkanes by the present procedure were unsuccessful. Branched-chain alkanes on the other hand were in general converted to a range of isomerization products many of which contained tritium. Thus the procedure would appear to be inferior to metal-catalyzed exchange methods[10] for alkanes in general.

The method usefully complements the Lewis acid tritiation procedure[2] where catalysts such as ethylaluminium chloride were utilized again in the presence of small amounts of highly tritiated water as isotope source. The zeolite method has the advantage that the isotope is incorporated with high specificity at sites active toward electrophilic substitution, while the alkylaluminum catalyzed systems yield randomly labeled aromatic centers.[3] Furthermore, the complication of intramolecular substituent shifts, as observed in the Lewis acid tritiation of disubstituted aromatics,[11] such as the bromotoluenes, appears to be absent from the zeolite procedure. Biphenyl formation does not accompany benzene exchange, in contrast to some noble metal exchange methods,[12] nor is there the complication of byproduct formation observed in radiation-induced exchange.[13] Thus the present simple one-step procedure represents a useful method of tritiating a wide range of aromatic and related molecules with high efficiency.

Acknowledgment. We thank the Australian Research Grants Committee and the Australian Institute of Nuclear Sciences and Engineering for their support of the research at the University of New South Wales.

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Synthesis and Characterization of a Nitrosyl, a Nitrido, and an Imido Carbonyl Cluster

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Reactions studied in light of the metal cluster-metal surface analogy[1] have concentrated on the reduction of carbon monoxide[2-5] and, to a lesser extent, other unsaturated derivatives, such as nitriles,[6] acetylenes,[7] and olefins.[8] We have discovered and present here some initial results pertinent to two other surface-catalyzed processes: (1) the reaction of carbon monoxide with nitric oxide to produce carbon dioxide and nitrous oxide[9] and (2) the hydrogenation of nitrogen.[10] During our evaluation of the synthesis and properties of nitrosyl carbonyl clusters, we reacted PPN-$[Fe(CO)_3(NO)]$[11] [PPN = bis(triphenylphosphin)iminium cation] with $Fe_3(CO)_{12}$ in order to obtain a tetrairon nitrosyl cluster. Instead, X-ray crystallography revealed the presence of the *nitrido*

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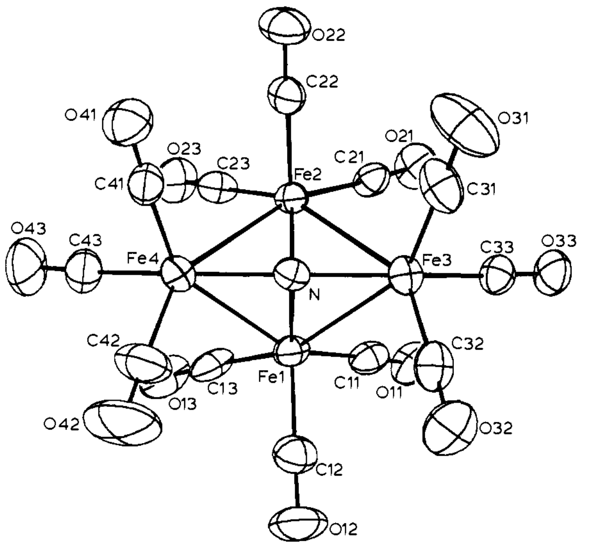


Figure 1. Perspective view of $[Fe_4N(CO)_{12}]^-$ looking down the pseudo-C_2 axis showing the disposition of the carbonyl ligands and the atom labels.

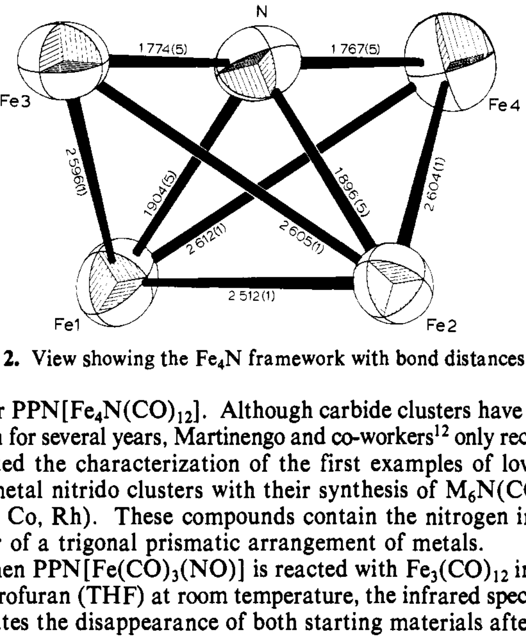


Figure 2. View showing the Fe_4N framework with bond distances in Å.

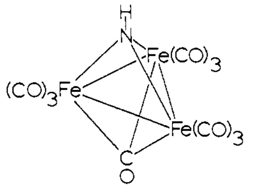
cluster $PPN[Fe_4N(CO)_{12}]$. Although carbide clusters have been known for several years, Martinengo and co-workers[12] only recently reported the characterization of the first examples of low-valent-metal nitrido clusters with their synthesis of $M_6N(CO)_{15}^-$ (M = Co, Rh). These compounds contain the nitrogen in the center of a trigonal prismatic arrangement of metals.

When $PPN[Fe(CO)_3(NO)]$ is reacted with $Fe_3(CO)_{12}$ in tetrahydrofuran (THF) at room temperature, the infrared spectrum indicates the disappearance of both starting materials after 1.5 h. The optimum stoichiometry is approximately 2 equiv of $PPN[Fe(CO)_3(NO)]$ to 3 equiv of $Fe_3(CO)_{12}$. When the solvent is removed from the reaction under vacuum, infrared analysis reveals the presence of a substantial quantity of $Fe(CO)_5$ in the distillate. Although the reaction appears to be complete by infrared spectroscopy, we have not yet obtained good recrystallized yields of $PPN[Fe_4N(CO)_{12}]$.[13] X-ray structural analysis[14] of black air-stable crystals obtained from an ether–hexane solution revealed that the irons were arranged in a butterfly configuration with the nitrogen bonded to all four metals (Figures 1 and 2). Three terminal carbonyl ligands are also bound to each iron atom. The overall symmetry closely corresponds to the point group C_{2v}. Some of the pertinent structural results are presented in Figure 2. The dihedral angle measured between the plane containing Fe1–Fe2–Fe3 and the one containing Fe1–Fe2–Fe4 is 78.2. The Fe3–N–Fe4 angle is essentially linear at 179.0 (3)°.

The molecule is structurally and electronically related to the fascinating series of iron carbide and η^2-CH clusters recently reported by Muetterties and co-workers.[5] The observed differences between the carbide cluster geometry and the nitrido cluster geometry appear to be related to the smaller size of the nitride ligand. Indeed, Muetterties and co-workers have prepared by a different method and characterized, using X-ray diffraction, the same tetrairon nitrido cluster in the protonated form.[15]

An important question regarding the fate of the oxygen atom originally bound to the nitrosyl ligand was answered by conducting the reaction in an evacuated tube followed by a mass spectral analysis of the gases. The mass peak at 44 indicated the presence of carbon dioxide. We are in the process of conducting the appropriate labeling studies to prove the origin of the CO_2.

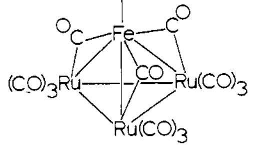
When $Na[Fe(CO)_3(NO)]$ is allowed to react with $Fe_3(CO)_{12}$, the infrared spectrum is consistent with the formation of $Na[Fe_4N(CO)_{12}]$.[16] Protonation with aqueous phosphoric acid results in the production of several compounds. The most abundant of these is $Fe_4N(CO)_{12}H$, which is isolated in 43% yield, and results from proton addition to the Fe1–Fe2 bond.[15] Although several of the remaining products have not yet been fully characterized, we have identified the new *imido* cluster $Fe_3(NH)(CO)_{10}$ (I).



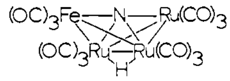
I

Spectroscopic evidence[17] reveals that this red crystalline air-stable species is isostructural with the known $Fe_3(NSiMe_3)(CO)_{10}$.[18] The ^1H NMR spectrum provides conclusive evidence that in the proposed structure the H is directly bonded to the N. The signal is observed at +9.5 ppm (δ) and shows three equally intense resonances due to coupling to the ^{14}N nuclei ($J_{^{14}N-^1H}$ = 57 Hz). Although the yield of $Fe_3(NH)(CO)_{10}$ is currently low (2%), conversion of a nitrido cluster into an imido cluster provides an interesting analogy to the heterogeneous hydrogenation of N_2.[10]

In contrast to the above chemistry, the reaction of $PPN[Fe(CO)_3(NO)]$ with $Ru_3(CO)_{12}$ produces $PPN[FeRu_3(CO)_{12}(NO)]$ (II) in 80% yield. This cluster was shown by crystallography[19]



II



III

to contain a tetrahedron of metals with the nitrosyl ligand being bound only to the iron in a linear fashion. Protonation of $PPN[FeRu_3(CO)_{12}(NO)]$ with CF_3COOH in CH_2Cl_2 results in loss of an oxygen atom as CO_2 and formation of $FeRu_3N(CO)_{12}H$,[20]

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[13] Anal. Calcd for $PPN[Fe_4N(CO)_{12}]$: C, 51.84; H, 2.72; N, 2.52. Found: C, 51.62; H, 2.79; N, 2.53.

[14] X-ray diffraction data for $PPN[Fe_4N(CO)_{12}]$: crystal system triclinic; space group $P\bar{1}$; a = 10.700 (2), b = 14.146 (3), c = 16.249 (3) Å; α = 91.15 (1), β = 94.55 (2), γ = 97.52 (2)°; volume = 2429 (2) Å^3; Z = 2; abs coeff = 13.3 cm^{-1}; diffractometer = Enraf-Nonius CAD4; radiation = graphite monochromatized Mo Kα; scan range = $0° \le 2\theta \le 50°$; reflections collected = 8544 total unique, 4001 with $F_o > 2.0\sigma F_o$; R = 0.054; Rw = 0.051.

[15] Tachikawa, M.; Stein, J.; Muetterties, E. L.; Teller, R. G.; Beno, M. A.; Gebert, E.; Williams, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 6648–6649.

[16] IR of $[Fe_4N(CO)_{12}]^-$: ν_{CO} (PPN^+, THF) 2016 s, 1991 vs, 1966 m, 1933 w; (Na, THF) 2016 s, 1990 vs, 1966 m, 1932 w.

[17] IR (ν_{CO}) 2094 w, 2051 vs, 2025 s, 1998 m, 1749 m cm^{-1} (hexane); (ν_{NH}) 3550 cm^{-1} ($CHCl_3$); mass spectrum, m/z 463 (parent), followed by 10 peaks each corresponding to a loss of a carbon monoxide. Anal. Calcd: C, 25.96; H, 0.22; N, 3.03. Found: C, 25.80; H, 0.20; N, 3.03.

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[19] X-ray diffraction data for $PPN[FeRu_3(CO)_{12}(NO)]$: crystal system monoclinic; space group $P2_{1/c}$; a = 19.690 (4), b = 16.262 (3), c = 15.911 (5) Å; β = 107.24 (2)°; volume = 4866 (4) Å^3; Z = 4; abs coeff = 13.3 cm^{-1}; diffractometer = Enraf-Nonius CAD4; radiation = graphite monochromatized Mo Kα; scan range = $0° \le 2\theta \le 50°$; reflections collected = 11698 unique, 7125 with $F_o > 3.0\ \sigma F_o$; R = 0.045; Rw = 0.068.

which can be readily isolated in 75% yield by solvent removal, extraction in hexane, and crystallization. The structure of this product (III) is very likely analogous to $Fe_4N(CO)_{12}H$, but the poor quality crystals were not suitable for X-ray crystallographic analysis. We are attempting to deprotonate and/or derivatize this cluster in order to clearly establish its structure.

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Supplementary Material Available: A listing of the positional and thermal parameters derived from the crystallographic analyses (7 pages). Ordering information is given on any current masthead page.

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(20) IR (ν_{CO}) 2104 w, 2071 s, 2062 s, 2043 s, 2029 s, 2000 m, 1991 m, 1968 w, 1955 w (hexane); mass spectrum, *m/z* 713 (parent) followed by peaks corresponding to stepwise loss of all the ligands. Anal. Calcd: C, 20.29; H, 0.14; N, 1.97. Found: C, 20.32; H, 0.15; N, 1.97.

Methane Activation. Photochemical Reaction of Copper Atoms in Solid Methane

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The activation of saturated hydrocarbons is of wide-ranging chemical and technological significance.[1,2] Methane chemistry, in particular, presents an important and timely challenge with ramifications for the future development of natural gas conversion processes. We report here a photosensitized reaction (320 nm) of copper atoms in methane matrices at 12 K, which produces CuH, CH_3, $CuCH_3$, and H atoms by a mechanism which appears to involve the photolytic decomposition of the intermediate $HCuCH_3$. Barrett et al.[3] have observed a reaction of methane with Fe_2 molecules but not with Fe atoms, and Hauge et al.[4a] have found that photolysis during deposition of Fe/CH_4 vapors causes iron atom insertion products to form. Billups et al. just reported the photoinsertion of several metal atoms into methane.[4b] Neither V atoms nor V_2 molecules react with saturated hydrocarbons in low-temperature matrices.[5]

The absorption spectrum of copper atoms isolated in solid methane is shown in trace A of Figure 1, and the course of the photosensitized reaction is illustrated in traces B and C. Photoexcitation of Cu[6] or Ag[7] atoms isolated in rare-gas matrices promotes diffusion and aggregation of the metal atoms, characterized by approximately second-order kinetics during the early stages of nucleation (Scheme I). In contrast, 320-nm photolysis of Cu/CH_4 matrices results in a rapid *first-order* decay of the atomic absorption bands with no apparent growth of Cu_2 or higher copper clusters but with the appearance of broad absorption features near 350, 220, and <200 nm (Figure 1C). Further evidence for photochemical reaction of copper atoms in methane matrices was obtained from fluorescence studies, which showed the characteristic $^2D \rightarrow {}^2S$ fluorescence of rare-gas matrix-isolated copper atoms[8] to be completely quenched in the case of methane matrices (Scheme I).

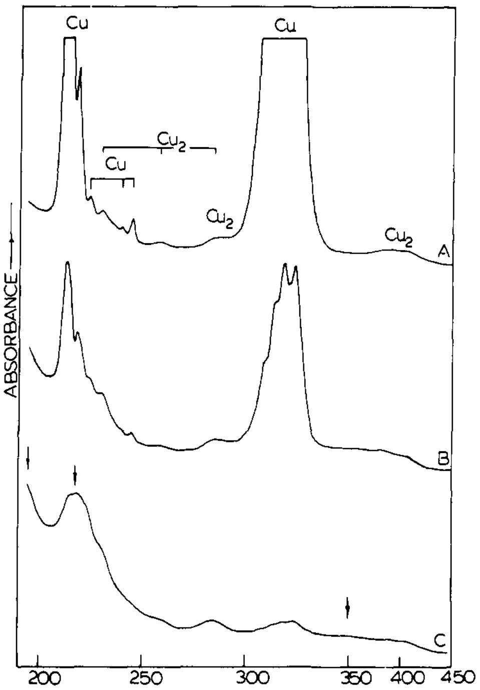

Figure 1. Absorption spectra of Cu atoms isolated in solid methane at 12 K ($Cu/CH_4 \simeq 1/10^4$), showing decay of the Cu atom bands and growth of new absorption features near 350, 220 and <200 nm as a result of 320-nm photolysis. (A) Freshly deposited matrix, (B) 1 min, 320-nm irradiation, (C) 15 min, 320-nm irradiation. Trace amounts of Cu_2 coisolated with Cu atoms are indicated. Arrows depict product absorptions (see text) which can be seen more clearly in higher density deposits.

Scheme I

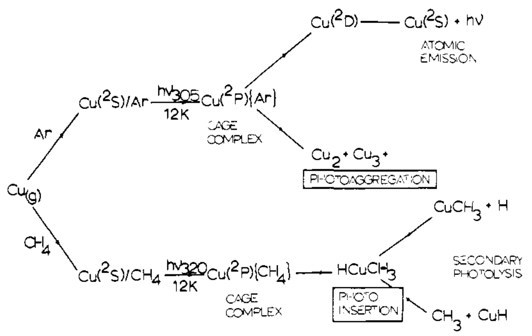

Figure 2 shows infrared spectra obtained at various stages during the Cu/CH_4 photochemical reaction, and Table I presents a summary of the major infrared bands found to grow in as a result of 320-nm copper atom photolysis. Additional bands observed below 600 cm^{-1} will be described in a separate paper. The strong bands at 1850 and 611 cm^{-1} are readily assigned to CuH[9] and CH_3[10,11] species, respectively, by comparison with known spectra.

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