Table I. Comparison of the Activity of Various Rhodium Catalysts[a]

Catalyst	Initial rate $\times 10^4$ (mol g-cata-lyst^{-1} min^{-1})	Rh content $\times 10^6$ (g-atom g-cata-lyst^{-1})	Activity (mol g-atom-Rh^{-1} min^{-1})	Activation energy (kcal mol^{-1})
1 SiO$_2$	5.3	3.3	160	7
2 SiO$_2$ without washing	5.8	45	13	7
3 SiO$_2$	7.0	4.0	175	—
4 SiO$_2$–Al$_2$O$_3$ (13 wt % Al$_2$O$_3$)	1.6	33	4.8	—
5 SiO$_2$–Al$_2$O$_3$ (23 wt % Al$_2$O$_3$)	1.3	33	4.0	—
6 Al$_2$O$_3$	0.03	63	0.04	—
7 Rh-Y zeolite[4]	0.8	250	0.3	—
8 RhCl$_3$ (in EtOH)	—	—	$\sim 10^{-2}$	13.6[3]
9 [(C$_2$H$_4$)$_2$RhCl]$_2$ (in EtOH)	—	—	$\sim 10^{-2}$	17.2,[1] 14.7[3]

[a] Experimental conditions: catalysts 1–6, initial ethylene pressure = 460 Torr at 25°C; catalyst 7, 200 Torr at 20°C; catalysts 8~9,[3] 3000 Torr at 35°C or catalyst 9,[1] 1100 Torr at 50°C.

compared in Table I, which shows that silica gel has a high promoting effect. The activity of rhodium chloride supported on silica gel is much higher than that of Rh–Y zeolite,[4] and it corresponds to about 10^4-fold increase from that found with homogeneous rhodium chloride catalysts.[1,3]

A comparison of catalyst 1 and catalyst 2, which were prepared with and without washing by methanol, gives important information about the catalyst. As can be seen from Table I, catalyst 2 and catalyst 1 have almost the same activity, although the rhodium content of the former is much higher. From ESCA spectroscopic study, it was found that most of the rhodium content of catalyst 2 is free rhodium chloride. This part, the free rhodium chloride, which is removed by washing, may not be effective in the dimerization. The effect of heat treatment of these two catalysts (in vacuo for 3 hr) on their activity for dimerization and propene hydrogenation was examined. The dimerization activity of both catalysts decreased rapidly on heating at about 150°C, and the color of the catalysts changed from red-orange to dark brown or black. However, the hydrogenation activity of the catalysts exhibited a different temperature dependence. Catalyst 2 was active for the hydrogenation at temperatures higher than 200°C, whereas catalyst 1 was inactive even at 400°C, in spite of its sufficient rhodium content. The ESCA spectrum of the hydrogenation active catalyst 2 showed a considerable amount of metallic rhodium, which was responsible for the hydrogenation activity. When carbon monoxide was introduced into the reaction system the initial rate of the dimerization decreased linearly with the amount of carbon monoxide introduced. The amount of carbon monoxide needed for complete inhibition was estimated as 3.5 × 10^{-6} (mol/g-catalyst), which is almost the same as the rhodium content of catalyst 1, 3.3 × 10^{-6} (g-atom/g-catalyst). Accordingly, the active rhodium species can be considered as highly dispersed in molecular form, not in clusters. The observed activation energy of the dimerization was 7 kcal/mole, which is about one-half of that obtained with the homogeneous catalysis. Silica gel, which had been treated with γ-aminopropyltriethoxysilane,[5] a strong reagent for surface hydroxyl of silica gel, did not show any promotional effect in the dimerization.

From these results, we have concluded that the active rhodium species of the supported catalysts is the surface compound (1) formed from rhodium chloride and the surface silanol according to the equation
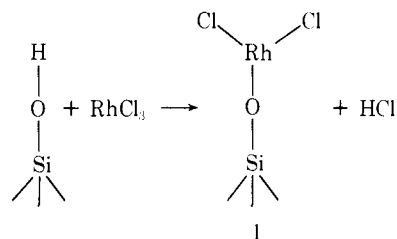
and the high dimerization activity is due to the ligand effect of Si–O– on Rh. The latter effect may be found in the enhancement of catalytic activity of silica supported transition metal complexes.[6,7]

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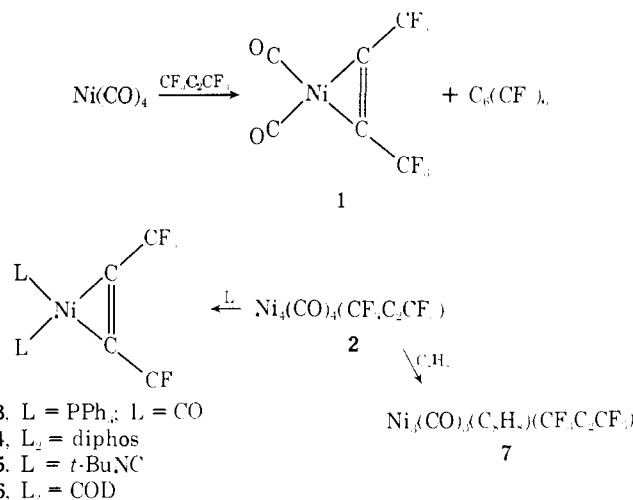Tokyo Institute of Technology
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Formation of Tetra- and Trinuclear Cluster Complexes from Tetracarbonylnickel and Hexafluorobut-2-yne. The Molecular Structures of [Ni$_4$(CO)$_4$(CF$_3$C$_2$CF$_3$)$_3$] and [Ni$_3$(CO)$_3$(CF$_3$C$_2$CF$_3$)(C$_8$H$_8$)]

Sir:

There is considerable interest in fluxional and chemically active metal cluster complexes in relation to their ability to provide multinuclear sites for the bonding of alkenes or alkynes. We wish to report the first example of a complex in which a triangular array of metal atoms is able to stabilize a planar cyclooctatetraene ligand.

Removal of carbon monoxide in the reaction (50°) of tetracarbonylnickel with hexafluorobut-2-yne (HFB) affords (see Scheme I) hexakistrifluoromethylbenzene and a colorless volatile liquid complex [Ni(CO)$_2$(CF$_3$C$_2$CF$_3$)] (1) (ν_{CO} (hexane) 2122 m, 2076 s, $\nu_{C\equiv C}$ 1905 w cm^{-1}; ^{19}F

Scheme I

3. L = PPh$_3$; L = CO
4. L$_2$ = diphos
5. L = t-BuNC
6. L$_2$ = COD
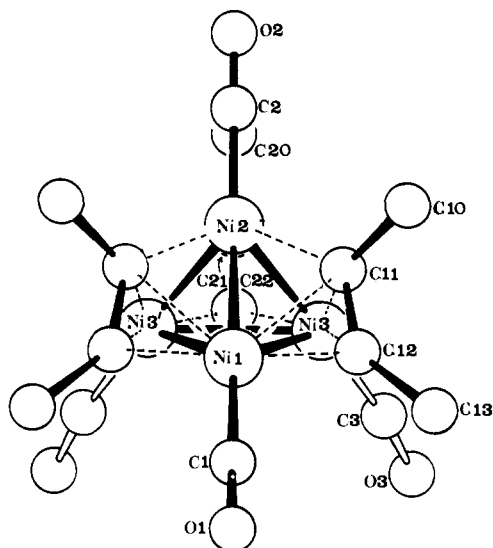
Figure 1. Molecular structure of [Ni$_4$(CO)$_4$(CF$_3$C$_2$CF$_3$)$_3$]. Fluorine atoms omitted for clarity. The Ni–CO bond distances average 1.81 (6) Å and the three Ni(apex)–Ni(basal)–CO fractions are each nearly linear. The three OC–Ni(apex)–Ni(basal) are each nonlinear with the OC–Ni(apex) vector nearly collinear with the idealized C_3 axis of the molecule.

NMR resonance (acetone-d_6; rel. CCl$_3$F) at 55.3 (s) ppm). At room temperature in an open system, complex 1 rapidly decomposes to give a dark purple tetranuclear species Ni$_4$(CO)$_4$(CF$_3$C$_2$CF$_3$)$_3$] (2) (ν_{CO} (hexane) 2115 s, 2102 s, 2091 sh, $\nu_{C\equiv C}$ 1564 w cm^{-1}; ^{19}F NMR resonances (acetone-d_6) at 53.6 (s) and 56.9 (s) ppm). An x-ray diffraction study on complex 2 (crystal data: C$_{16}$Ni$_4$F$_{18}$O$_4$, M = 883.0, monoclinic, P2$_1$/m, a = 8.506 (2), b = 16.05 (1), c = 9.011 (4) Å, β = 100.52 (3)°, U = 1210 (1) Å^3, Z = 2, d_c = 2.286 g cm^{-3}, μ(Mo K$\bar{\alpha}$) = 30.4 cm^{-1}, θ–2θ scan, 2.9° ⩽ 2θ ⩽ 50.0°, R = 0.12 for 1033 independent observed reflections (Syntex P2$_1$ diffractometer) from a rapidly decaying crystal, full matrix least-squares, Ni, F atoms anisotropic, all data given unit weight) revealed the molecular structure shown in Figure 1.[1] The atoms Ni(1,2), C(1,2,20,21,22,23), O(1,2) [and two fluorine atoms] lie on a crystallographic mirror plane. The geometry of the metal cluster is that of a trigonal pyramid (local C_{3v} symmetry) with nickel atoms 1, 3, and 3′ in basal positions. The independent basal–basal separations are both 2.669 Å, ±0.007 [Ni(1)–Ni(3)], ±0.010 [Ni(3)–Ni(3′)], while apical–basal distances are 2.369 (8) Å to Ni(1) and 2.385 (7) Å to Ni(3). The geometry of the individual HFB ligands coordinated onto the triangulated metal faces is very similar to that observed[3] in [Fe$_3$(CO)$_9$(PhC$_2$Ph)]. Bonding separations between metal and carbon atoms are Ni(2)–C(11), 1.98; Ni(2)–C(21), 1.98; Ni(1)–C(11), 2.21; Ni(1)–C(12), 1.95; Ni(3)–C(11), 2.15; Ni(3)–C(12), 1.98; Ni(3)–c(21), 2.20; Ni(3)–C(22), 1.94, all ±0.03 Å, and are complemented by C–C–C angles averaging 129°. Nonbonding distances include Ni(2)⋯C(12), 2.82 (3) and Ni(2)⋯C(22), 2.83 (5) Å. These parameters suggest formal σ-bonding between Ni(2) and C(11) and C(21), and the association of each basal nickel with all four adjacent carbons in three-center μ-bonds. In spite of the relatively short C(11)–C(12) and C(21)–C(22) separations observed, 1.33 (7) and 1.28 (4) Å, respectively, each acetylenic ligand could, therefore, donate up to four electrons, allowing the cluster as a whole to adopt a closed-shell configuration. A novel tetranuclear nickel cluster [Ni$_4$(t-BuNC)$_7$] has recently been reported[4] and shown to contain terminal, as well as "edge-bridging" and "face-bridging" isocyanide ligands.
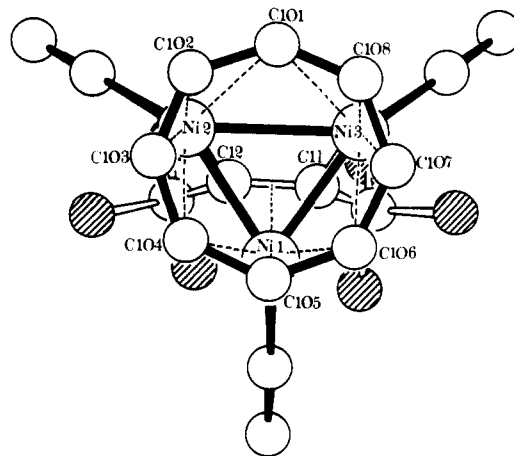

Figure 2. Molecular structure of [Ni$_3$(CO)$_3$(C$_8$H$_8$)(CF$_3$C$_2$CF$_3$)]. The Ni–CO distances average 1.78 (1) Å, with the carbonyl groups bent ca. 30° out of the Ni$_3$ plane away from the C$_8$ ring.

At room temperature in hexane 2 slowly reverts, with some decomposition, to the mononuclear complex 1. However, addition of triphenylphosphine, 1,2-diphenylphosphinoethane, tert-butylisocyanide, or cycloocta-1,5-diene gave respectively the crystalline mononuclear complexes 3 (ν_{CO} (hexane) 2052 s, $\nu_{C\equiv C}$ 1852 w, 1834 w cm^{-1}), 4 (^{19}F NMR resonance at 53.5 ppm (t, J_{PF} = 4.4 Hz)], 5 (ν_{NC} (hexane) 2158 m, 2125 s, $\nu_{C\equiv C}$ 1848 w, 1825 w cm^{-1}), and 6 ($\nu_{C\equiv C}$ 1846 w, 1828 w cm^{-1}). Whereas these reactions give mononuclear complexes, the corresponding reaction of 2 with cyclooctatetraene affords a black crystalline trinuclear complex [Ni$_3$(CO)$_3$(C$_8$H$_8$)(CF$_3$C$_2$CF$_3$)] (7) (ν_{CO} (hexane) 2065 m, 2047 vs, 2040 vs cm^{-1}; ^{19}F resonance at 55.9 ppm (s), ^{1}H resonance (CDCl$_3$) at τ 5.5 (s)). In order to elucidate the molecular structure a single-crystal x-ray diffraction study was undertaken (crystal data: C$_{15}$H$_8$Ni$_3$F$_6$O$_3$, M = 526.4, monoclinic P2$_1$/n, a = 9.591 (2), b = 11.994 (3), c = 14.876 (4) Å, β = 99.57 (2)°, U = 1687.5 (7) Å^3, Z = 4, d_c = 2.071 g cm^{-3}, μ(Mo Kα) = 33.8 cm^{-1}, θ–2θ scan, 2.9° ⩽ 2θ ⩽ 50.0°, R = currently 0.054 for 2114 reflections, full-matrix least-squares, Ni, F, (CO) atoms anisotropic, unit weights).

The Ni$_3$ species (Figure 2) comprises an isosceles triangle (Ni(1)–Ni(2), Ni(1)–Ni(3), 2.458(2) Å; Ni(2)–Ni(3), 2.703(2) Å) of metal atoms, each carrying a terminal carbonyl group, sandwiched between a single HFB ligand and a η^8 (with respect to the Ni$_3$ triangle) cyclooctatetraene bonded ring. The latter is planar to within 0.08 Å and very nearly coplanar with the metal triangle (dihedral angle ca. 3.0°). An effective mirror plane through atoms C(101), Ni(1), and C(105) bisects the molecule. Atoms Ni(2) and Ni(3) bind C(12) and C(11) at 1.901 (8) and 1.895 (9) Å, respectively, and lie only +0.39 Å (mean) out of the acetylenic C$_4$ plane; Ni(1), an average 2.004 (8) Å from C(11) and C(12), is displaced −1.55 Å from this plane. Such geometry has previously been described, for [Fe$_3$(CO)$_8$(PhC$_2$Ph)] (violet isomer)[5] and [Os$_3$(CO)$_7$(PhC$_2$Ph)(Ph$_4$C$_4$)],[6] in terms of essentially σ-bonding between carbon and equivalent metal atoms (Ni(2) and Ni(3)) accompanied π-donation from the olefinic fragment to the third metal atom Ni(1). In the present compound the C(11) and C(12) separation, 1.38 (1) Å, and C–C–C angles, 126.3 (8)°, are consistent with such a four-electron donor model.

The Ni–C (ring) bond distances fall into three distinct groups: short, 2.011 (10)–2.105 (10) Å, exemplified by Ni(1)–C(105), Ni(2)–C(102,103), Ni(3)–C(107,108); intermediate, 2.368 (9), 2.332 (11) Å, Ni(1)–C(104,106); and long

2.549(10)–2.596(11) Å, Ni(2)–C(101,104), Ni(3)–(101,106). Further, the maximum variation in C–C distances (mean 1.433(16) Å) around the ring is less than 2σ.

Thus, the C_8-ring to metal bonding is highly delocalized and in terms of valence bond theory the bonding may be represented by resonance between the cannonical forms (A) and (B) (Scheme II). This is consistent with the observed

Scheme II

A   B
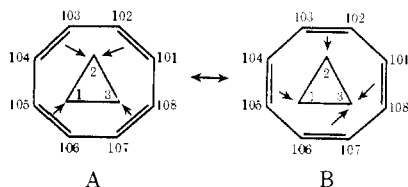
molecular parameters and allows each metal atom access to 18 electrons. Since the ^1H NMR spectrum shows only a singlet resonance even at $-90°C$, it is evident that an unusual fluxional process occurs in solution.

It is likely that in the formation of 7 from the Ni_4 cluster the cyclooctatetraene ligand becomes bonded to the rela-

tively open Ni(1)Ni(3′)Ni(3) triangular face, suggesting that 2 might provide a template in a catalytic reaction.

References and Notes

(1) It has been previously reported[2] that [Ni(CO)₄] and HFB react to give [Ni₄(CO)₃(CF₃C₂CF₃)₃], the molecular formula being inferred from mass spectrometry. The x-ray diffraction study reveals the presence of the fourth terminal CO ligand so that the cluster as a whole obeys the "18-electron" rule.
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Book Reviews

The Botany and Chemistry of Hallucinogens. By R. E. SCHULTES (Harvard University) and A. HOFMANN. Charles C. Thomas Publishers, Springfield, Ill. 1973. xxii + 267 pp. $14.75.

This is not only a unique and definitive volume on the botanical classification and chemical composition of hallucinogenic plants but also a fascinating history of their use by aboriginal societies and an excellent source of information of their psychoactive and toxic effects. It contains five chapters: Hallucinogenic or Psychomimetic Agents: What are they?, The Botanical Distribution of Hallucinogens, The Chemical Distribution of Hallucinogens, Plants of Hallucinogenic Use, and Plants of Possible or Suspected Hallucinogenic Use. By far the longest chapter (177 pp) gives a botanical description of each species, its history, psychoactive effects, and chemical constituents. The book is exquisitely produced and liberally sprinkled with ancient illustrations of plants and photographs of aboriginal plant collectors. For the researcher, this volume is indispensable; for the teacher of undergraduate organic classes, it will yield many anecdotes with which to spice up lectures; for the interested chemist, it will provide informative and enjoyable reading.

Victor Snieckus, *University of Waterloo*

Analysis of Water. Fifth Edition. (Translation from French). By J. RODIER and collaborators (formerly associated with the Institut d'Hygiène du Maroc and several other institutions). John Wiley & Sons, New York, N.Y. 1975. xviii + 926 pp. $82.50.

This is an encyclopedic work of reference covering *all* aspects of the analysis of water. This is a really old-fashioned book depending almost entirely on gravimetric, volumetric, colorimetric, and related classical forms of qualitative and quantitative analyses, although some sections also contain data obtained by polarography and the atomic absorption method of analysis. One of the appendixes gives a synoptic survey of some of the more recent methods of instrumental analysis, although results obtained by these methods are not quoted to any appreciable extent within the text. Almost all the references are taken from obscure French publications and governmental circulars and tend to incline heavily toward less modern publications. The book, therefore, is rather out of date and is not of much value either in research or in teaching. The volume

is extremely useful, however, to technologists undertaking analysis of water in less equipped laboratories and with limited training in modern instrumental analysis. Also, it is a mine of comprehensive information on several less common, and even quite obscure, problems of water analysis. For technologists engaged in the problems of the analysis of water, the material in the book would be quite useful since established analytical procedures, however ancient, never loose their general validity.

Ashok K. Vijh, *Hydro-Quebec Institute of Research*

Proceedings of the International Symposium on Nitrite in Meat Products. Edited by B. KROL and B. J. TINBERGEN. Centre for Agricultural Publishing and Documentation, Wageningen, The Netherlands. 1974. 268 pp. $18.00.

This book is a collection of papers presented at the International Symposium on Nitrite in Meat Products held at Zeist, The Netherlands, September 10-14, 1973. The analytical, microbiological, chemical, technological, and toxicological aspects of the problem were considered.

Six resolutions based on the symposium work were accepted by the participants. The second states: "All relevant information indicates that nitrite is currently an indispensable inhibitor of pathogenic microorganisms (*Clostridium botulinum*) in many meat products. In addition nitrite plays a key role in colour formation and flavour development. No adequate substitute is yet known." Since the date of the symposium, it has been reported that formaldehyde catalyzes the nitrosation of amines at physiological pH's. In view of the carcinogenicity of the nitroso amines, it would appear that other methods of preservation should be investigated. As a spur to such efforts, some consumers might want to avoid nitrite-preserved meats.

Emil H. White, *The Johns Hopkins University*

Microcrystalline Polymer Science. By O. A. BATTISTA (Research Services Corp.). McGraw-Hill, New York, N.Y. 1975. x + 208 pp. $18.50.

Dr. Battista explains microcrystalline polymer science in Chapter 1 (16 pp) and discusses then the preparation, properties, and application of microcrystals from cellulose (41 pp), collagen (60