infra) were sufficient to characterize the almost CH_2Cl_2 insoluble species as $W(\eta^5\text{-}C_5Me_5)Cl_4$ (yield ~80%). We presume that it is a dimer by analogy with $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$,[3] and in accord with the compound's insolubility. $W(\eta^5\text{-}C_5Me_5)Cl_4$ will react readily with NEt_4Cl in dichloromethane to give brown, crystalline $[NEt_4][W(\eta^5\text{-}C_5Me_5)Cl_5]$[6b] and with PMe_3 to form toluene-soluble, green, crystalline $W(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$.[6c] $W(\eta^5\text{-}C_5Me_5)Cl_4$ and its PMe_3 adduct have signals in their EPR spectra in dichloromethane at 25 °C at $g = 1.92$ and $g = 1.90$, respectively, with half-height widths of 50 and 64 G, respectively.

An analogous reaction between $Mo(\eta^5\text{-}C_5Me_5)(CO)_3Me$[7] and PCl_5 in dichloromethane yields a purple solution from which microcrystalline purple $Mo(\eta^5\text{-}C_5Me_5)Cl_4$ can be isolated in ≳90% yield.[8a] Chloride ion will not add to the metal to give a stable complex of the type $[Et_4N][Mo(\eta^5\text{-}C_5Me_5)Cl_5]$, but trimethylphosphine will add to give purple $Mo(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$.[8b] EPR spectra of $Mo(\eta^5\text{-}C_5Me_5)Cl_4$ and $Mo(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$ in THF at 25 °C show relatively narrow peaks (half-height width ≈ 7 G) at $g = 1.99$ and 1.97, respectively, with couplings of 39 and 45 G to ^{97}Mo ($S = ^5/_2$) and ^{95}Mo ($S = ^5/_2$) and of ~27 G to ^{31}P in the case of $Mo(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$.

$W(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$ reacts smoothly with excess dimethylzinc in toluene to give a yellow, crystalline, paramagnetic complex ($g \approx 2$ in pentane at 25 °C) in good yield (~80%) that analyzes as $W(\eta^5\text{-}C_5Me_5)Me_4$.[9] An X-ray structural study of $W(\eta^5\text{-}C_5Et_3Me_2)Me_4$[10] confirms that the formulation is correct, that the molecule is a monomer and that the geometry is square pyramidal. $W(\eta^5\text{-}C_5Me_5)Cl_4$ reacts similarly with dimethylzinc, but the yield of $W(\eta^5\text{-}C_5Me_5)Me_4$ is only ~40%. So far we have not been able to prepare $Mo(\eta^5\text{-}C_5Me_5)Me_4$ in a similar manner.

One of the main reasons for developing the $W(\eta^5\text{-}C_5Me_5)Cl_4$ and $W(\eta^5\text{-}C_5Me_5)Me_4$ chemistry was in order to prepare and structurally characterize what we expected to be more crystalline complexes analogous to $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_4]_2$ and $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_3]_3$.[11] $W(\eta^5\text{-}C_5Me_5)Me_4$ reacts with H_2 at 1000 psig in pentane to yield a mixture of two hydride complexes having signals at −0.34 ($J_{HW} = 33$ Hz) and −1.65 ppm (br), respectively (cf. −0.81 and −1.86 ppm for the $\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu$ species above). ^1H NMR spectra of poorly crystalline samples of $[W(\eta^5\text{-}C_5Me_5)H_4]_2$ (obtained in ~25% yield by selective crystallization from pentane) show the expected hydride signal and ^{183}W satellite intensities (cf. the $\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu$ derivative[11]). The peak at −1.65 ppm in the mixture is assigned to $[W(\eta^5\text{-}C_5Me_5)H_3]_3$, the broadening being due to the slowing of a fluxional process that interconverts all hydride ligands (cf. $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_3]_3$[11]). These results suggest that the above approach to hydride complexes will be generally successful for peralkylated cyclopentadienyl complexes.

We have not yet seen any reactions in the literature in which a transition-metal complex is chlorinated by PCl_5 and therefore are curious as to whether this type of reaction might be more generally useful for preparing other mono($\eta^5\text{-}C_5Me_5$) complexes, e.g., $Re(\eta^5\text{-}C_5Me_5)Cl_4$. We also are now able to explore the chemistry of $M(\eta^5\text{-}C_5Me_5)Cl_4$ (M = Mo, W) in more detail, in particular with respect to formation of alkyl and hydrido complexes.

Acknowledgment. This work has been supported by the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC02-78ER04949-A003. L.B. thanks the Sohio Corp. for a graduate fellowship during the academic year 1983–1984.

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[8] (a) A solution of $Mo(\eta^5\text{-}C_5Me_5)(CO)_3Me$ (10 g) dissolved in 40 mL of dichloromethane was added to 16 g of PCl_5 partially dissolved in 200 ml of dichloromethane. Gas evolved and the solution turned purple. The solution was refluxed for 12 h, cooled, and filtered to give ~10.5 g of the intensely purple, microcrystalline product (~95% yield). Anal. Calcd for $MoC_{10}H_{15}Cl_4$: C, 32.20; H, 4.06; Cl, 38.02. Found: C, 32.03; H, 3.96; Cl, 37.31. (b) Anal. Calcd for $MoC_{13}H_{24}Cl_4P$: C, 34.77; H, 5.40; Cl, 31.58. Found: C, 35.35; H, 5.45; Cl, 31.61.

[9] Anal. Calcd for $WC_{14}H_{27}$: C, 44.34; H, 7.18. Found: C, 44.01; H, 6.66; Cl, ≲0.5.

[10] See footnote 12 and supplementary material in ref 3.

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Nickel–Nickel Dimers: The Synthesis and Novel Structure of $[Ni_2(\mu\text{-}CNMe)(CNMe)_3(PPh_2CH_2PPh_2)_2][PF_6]_2$

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Summary: Conproportionation of $[Ni^{II}(CNMe)_4][PF_6]_2$ with $Ni^0(CNMe)_4$ results in formation of the new binuclear Ni^I complex $[Ni^I{}_2(CNMe)_8][PF_6]_2$, **1**. Reaction of **1** with bis(diphenylphosphino)methane (dppm) yields the novel, asymmetrically bridged complex $[Ni_2(\mu\text{-}CNMe)(CNMe)_3(dppm)_2][PF_6]_2\cdot CH_2Cl_2$, **2**. The structure of **2** as a solid has been determined by X-ray diffraction. In solution, **2** is fluxional and variable-temperature $^{31}P\{^1H\}$ NMR studies indicate rapid interconversion of the asymmetric structure of **2** above −45 °C.

While there exists a rich organometallic and catalytic chemistry of nickel,[1] the chemistry of direct Ni–Ni bonds has received relatively little attention. In the course of our studies of the chemistry and photochemistry of the metal–metal bonds of binuclear Pd(I) and Pt(I) complexes,[2-6] we sought to examine the corresponding properties of bonds between Ni(I) ions. We report herein the synthesis of new binuclear nickel complexes which display a range of unusual Ni–Ni interactions. The unprecedented structure of a bis(diphenylphosphino)methane (dppm) bridged complex is also described as well as preliminary studies of its chemistry.

The new binuclear Ni(I) isocyanide complex $[Ni_2^I(CNMe)_8][PF_6]_2$, **1**, was prepared by conproportionation

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[‡] Address correspondence pertaining to crystallographic studies to this author.

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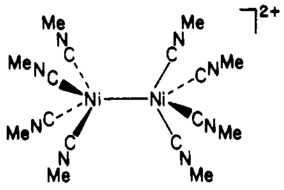
of $[Ni^{II}(CNMe)_4][PF_6]_2$[7] and $Ni^0(CNMe)_4$[8] in CH_2Cl_2 at 0 °C. Conproportionation of formally zerovalent and divalent Ni, Pd, and Pt complexes has been proven a viable synthetic route to binuclear, M–M bonded complexes of these metals.[9] Complex **1**[10] is obtained in 92% yield as deep purple crystals which are diamagnetic by the Evan's method.[11] In solution, complex **1** is EPR silent to +50 °C. The ^1H NMR of **1** indicates only one methyl isocyanide environment to −70 °C. There is, however, a marked temperature dependence of both the chemical shift and line width of the observed ^1H NMR signal. Over the temperature range +35 to −50 °C, the ^1H NMR chemical shift of **1** varies from δ 3.92 to 3.30 while the apparent line width decreases from 14 to 3 Hz. No noticeable variation in either chemical shift or line width occurs below −50 °C. The observed equivalence of the methyl isocyanide ligands of **1** together with analytical and magnetic data suggest that below −50 °C **1** is a spin-paired binuclear, formally Ni(I) complex. We thus propose a symmetric structure for **1**. The temperature-dependent chemical shift and line width observed in the ^1H NMR of **1** indicate a Ni–Ni bond which is thermally labile by homolytic or heterolytic processes to give traces of paramagnetic Ni^I or Ni^{II}, respectively.



1

The reaction of **1** with bis(diphenylphosphino)methane was employed to sequester the two metal centers in an intact binuclear structure. The reaction with dppm in CH_2Cl_2 affords $[Ni_2(CNMe)_4(dppm)_2][PF_6]_2{\cdot}CH_2Cl_2$, **2**, as deep purple crystals in 82% yield.[12] Complex **2** exhibits a broad ν(CN) band at 2200 cm^{-1} and an even broader band at 1825 cm^{-1}. In contrast to **1**, we find no evidence of a paramagnetic contribution to the ^1H or $^{31}P\{^1H\}$ NMR chemical shifts of **2**. At −10 °C the $^{31}P\{^1H\}$ NMR spectrum of **2** consists of a single resonance. As the temperature is lowered, however, the signal broadens until at −64 °C a distinct AA′XX′ $^{31}P\{^1H\}$ NMR spectrum is evident. The exchange rate constant $k_{ex} = (\pi/2)\Delta\nu$ and coalescence free energy $\Delta G_c^{\ddagger}$ have been estimated to be 4.3×10^3 s^{-1} and ~10 kcal/mol at −45 °C, respectively.[23] The 28-ppm wide AA′XX′ limiting low-temperature spectrum indicates two grossly different phosphorus environments and an asymmetric structure of **2**. We note that the simple substitution of four MeNC ligands of **1** by two bridging dppm ligands would be expected to give a symmetric structure, I, and that the loss of another MeNC ligand from I would likely give an A-frame type structure, II. A palladium complex of type II, $[Pd_2(\mu\text{-CNMe})(CNMe)_2(dppm)_2]^{2+}$, was reported by Balch and co-workers in 1977.[14] Neither structure I nor II however can accomodate the low-temperature $^{31}P\{^1H\}$ NMR and analytical data for **2**; and hence the crystal and molecular structure was determined by X-ray diffraction.[13]

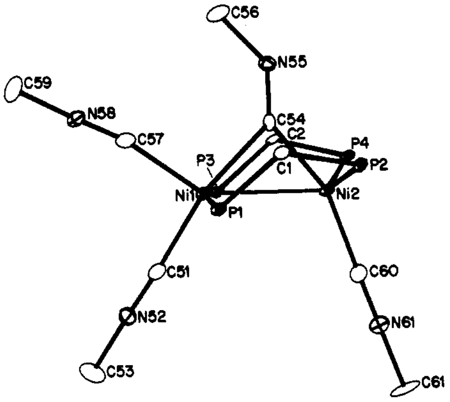
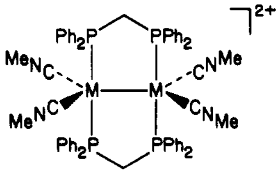
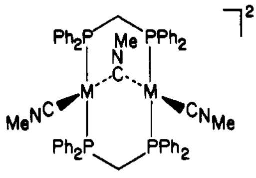


Figure 1. ORTEP drawing of the $[Ni_2(\mu\text{-CNMe})(CNMe)_3(dppm)_2]^{2+}$ cation without phenyl rings.



I



II

The crystal structure of **2** is composed of discrete $[Ni_2(CNMe)_4(dppm)_2]^{2+}$ molecular cations, two isolated PF_6^- anions, and one CH_2Cl_2 solvent of crystallization. An ORTEP drawing of the molecular cation $[Ni_2(CNMe)_4(dppm)_2]^{2+}$ without phenyl rings is presented in Figure 1. The structure of **2** is without precedent both in nickel

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(10) $[Ni_2(CNMe)_8][PF_6]_2$ (**1**): ^1H NMR (CD_2Cl_2) δ 3.30 (s) at −50 °C, 3.92 (s) at 35 °C; IR (Nujol) ν(CN) 2200 cm^{-1}; UV–vis (λ_{max}, nm (ϵ)) 304 (13000), 542 (516). Anal. Calcd for $C_8H_{12}N_4NiPF_6$: C, 26.11; H, 3.26; N, 15.23. Found: C, 26.33; H, 3.38; N, 15.51.

(11) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(12) $[Ni_2(CNMe)_4(dppm)_2][PF_6]_2{\cdot}CH_2Cl_2$ (**2**): ^1H NMR (CD_2Cl_2) δ 7.33 (m, 40 H), 3.33 (s, 4 H), 2.88 (s, 12 H); $^{31}P\{^1H\}$ NMR (H_3PO_4 external, CD_2Cl_2/CH_2Cl_2) δ 35.92 (m); IR (Nujol) ν(CN) 2200, 1825 cm^{-1}; UV–vis (λ_{max}, nm (ϵ)) 302 (24000), 576 (3190). Anal. Calcd for $C_{59}H_{58}N_4Ni_2Cl_2P_6F_{12}$: C, 49.72; H, 4.10; N, 3.93; P, 13.06. Found: C, 49.54; H, 4.05; N, 3.71; P, 14.52.

(13) Complex **2** crystallized in space group $P2_1/n$ with a = 12.425 (3) Å, b = 23.540 (8) Å, c = 21.536 (7) Å, β = 97.42 (2)°, Z = 4, ρ_{calcd} = 1.516 g/cm^3, and ρ_{obsd} = 1.53 (1) g/cm^3 for the formula unit $Ni_2Cl_2P_6F_{12}N_4C_{59}H_{58}$. Intensity data were collected at −140 °C using Cu Kα radiation (λ = 1.54184 Å) by the ω–2θ scan technique in the range $2° < 2\theta < 120°$ on a locally modified Enraf-Nonius CAD-4 diffractometer. A total of 9233 unique reflections from the octants (hkl) and ($hk\bar{l}$) were obtained. Three standard reflections were monitored every 120 min and showed no statistical variation over the course of data collection. The structure was solved by MULTAN–least squares–Fourier methods and is refined to R_1 and R_2 values of 0.060 and 0.085, respectively, for 766 parameters and 8868 observations with $F^2 > 2\sigma(F^2)$. Hydrogen atoms were located and added to structure factor calculations, but their positions were not refined. The linear absorption coefficient μ = 37.1 cm^{-1}, and an empirical absorption correction based on a series of psi scans was applied to the data. The estimated maximum and minimum T are 0.719 and 1.00, respectively. The quantities minimized were $R_1 = \sum[|F_o| - |F_c|)/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ where $w = 4F_o^2/\sigma^2(F_3^2)$. The esd of an observation of unit weight is 3.05. The programs used to solve the structure were part of the Structure Determination Package of B. A. Frenz and Associates, College Station, TX, and Enraf-Nonius, Delft, Holland. All calculations were performed on a DEC 11/60 computer in the Purdue University Department of Chemistry X-ray Diffraction Facility. Tables including a summary of crystal data and conditions for intensity data collection, positional parameters with esds, general temperature factor expressions, bond distances and angles, torsion angles, and observed and calculated structure factors are found in the supplementary section of this paper.

(14) Olmstead, M. M.; Hope, H.; Benner. L. S.; Balch, A. L. *J. Am. Chem. Soc.* 1977, *99*, 5502.

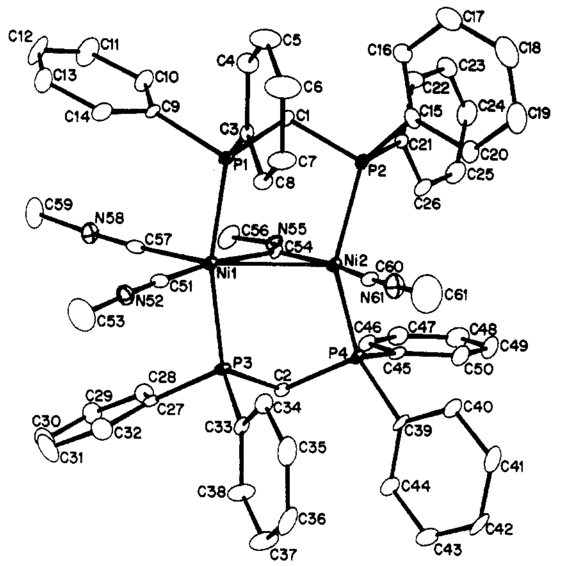
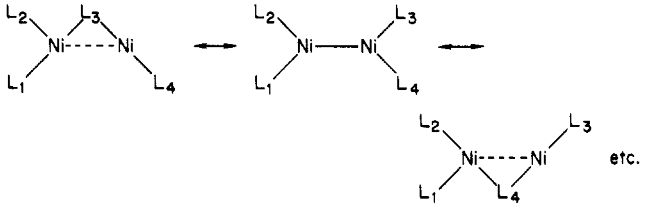


Figure 2. ORTEP drawing of the $[Ni_2(\mu\text{-}CNMe)(CNMe)_3(dppm)_2]^{2+}$ cation with all non-hydrogen atoms.

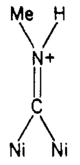
chemistry and in the chemistry of diphosphine-bridged binuclear complexes. The most striking aspect is the vast difference in the coordination geometries about each of the two nickel atoms. The two bridging dppm phosphorus atoms, and the bridging and two terminal MeNC ligands form an idealized square-based pyramid at Ni1 (∠C51–Ni1–C54 = 167.6 (2)°; ∠C57–Ni1–P1 = 95.7 (1)°; ∠C57–Ni1–P3 = 101.2 (1)°; ∠C57–Ni1–C54 = 98.6 (2)°; ∠C57–Ni1–C51 = 93.8 (2)°). The coordination geometry about Ni2, on the other hand, is probably best described as distorted trigonal bipyramidal, where the three equatorial sites are occupied by the two dppm phosphorus atoms P2 and P4 and the other nickel atom Ni1. Interestingly the bond lengths between Ni2 and both the bridging and terminal methyl isocyanide carbon atoms Ni2–C54 and Ni2–C60 are identical within experimental error (average 1.866 (4) Å). The bridging MeNC ligand is also quite asymmetric with bond lengths Ni1–C54 = 2.028 (4) Å and Ni2–C54 = 1.867 (4) Å and ∠Ni1–C54–Ni2 = 83.3 (2)°. The two dppm ligands are nearly trans at Ni1, ∠P1–Ni1–P3 = 163.05 (5)°, but are much more narrowly separated at Ni2, ∠P2–Ni2–P4 = 135.95 (5)°. The "trans–cis" dppm bonding and overall pseudoboat conformation of the eight-membered $Ni_2P_4C_2$ ring is unusual, but not unique. The "non-A-frame" $Rh_2(\mu\text{-}CO)(CO)_2(dppm)_2$,[15] as well as $Rh_2(CO)Cl_2(P(OPh)_2NEt\ P(OPh)_2)_2$,[24] and $[Pt_2Me_3(dppm)_2]^+$,[25] have recently been found to contain bridging dppm ligands trans at one metal and cis at the other. The Ni1–Ni2 separation of 2.5924 (9) Å is significantly longer than that typically attributed to direct Ni–Ni bonds (2.29–2.58 Å).[16-22] A complete view of the $[Ni_2(\mu\text{-}CNMe)(CNMe)_3(dppm)]^{2+}$ molecular cation including phenyl rings is given in Figure 2.

The structure of **2** is probably best viewed as an exo MeNC adduct of a Ni(I) A-frame of structure II. The added exo isocyanide creates an 18 electron Ni(I) center at Ni1, leaving a 16-electron configuration at Ni2. The Ni1→Ni2 interaction thus may be viewed as dative coordinate in character.[27,28] The variable-temperature $^{31}P\{^1H\}$ NMR spectra of **2** suggest that the asymmetric bonding in **2** is equilibrated at temperature above −45 °C. The simplest intramolecular mechanism which renders the phosphorus environments equivalent is a stepwise rotation of the four isocyanide ligands about the two nickel atoms through a symmetric intermediate (structure I).



An alternative mechanism involving dissociation of the exo MeNC and its reassociation at either of the exo sites is also consistent with the variable-temperature data. It is intriguing that **2** attains an asymmetric structure with an apparent donor/acceptor interaction between the nickel atoms, while **1** maintains a completely symmetric structure as determined by NMR to −70 °C.

Preliminary chemical studies suggest **2** is reactive toward both H^+ and H^-. The protonation of **2** with $[HOEt_2][BF_4]$ in CH_2Cl_2 leads to complex **3** and apparent N-protonation of the bridging isocyanide.[26] The reaction is accompanied by replacement of the ν(CN) band for the μ-CNMe of **2** by a new band at 1695 cm^{-1}. No evidence for a hydride is obtained, however, a new signal at δ 1.27 is evident in the ^1H NMR spectrum of **3**. The analytical, IR, and NMR data are consistent with N-protonation of the μ-CNMe ligand to give a μ-*N*-methyliminium species, III. Grundy and Robertson have recently demonstrated the facility of N-protonation and alkylation in dppm-bridged μ-CNR platinum complexes.[29] Complex **2** also exhibits reactivity toward H^- and CO_2. Results of our ongoing studies of **3** and the chemistry of **2** with H^- and CO_2 will be reported separately. It is clear that the chemistry of Ni(I) holds intriguing surprises in the way two nickels make a dimer.



III

Acknowledgment. This work was supported by the National Science Foundation (CHE-8411836) and the U.S. Department of Energy (DE-FG22-84PL70791). D.L.D. wishes to acknowledge a David Ross Fellowship. The PDP 11/34 computer and X-ray Structure Solution Package in

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(26) $[Ni_2(CNMeH)(CNMe)_3(dppm)_2][BF_4][PF_6]_2 \cdot Et_2O$ (**3**) is obtained as bright yellow crystals in 67% yield by addition of 1 equiv of $[HOEt_2][BF_4]$ to **2** in CH_2Cl_2: IR (CH_2Cl_2) ν(CN) 2245, 1695 cm^{-1}; ^1H NMR δ 7.50 (m, 40H), 3.4 (m, 4 H, Et_2O solvent), 3.05 (br, 12 H), 2.80 (m, 4 H), δ 1.27 (s, 1 H), 1.30 (t, (6 H, Et_2O solvent, overlapped).

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the Department of Chemistry were purchased with funds from the NSF Chemical Instrumentation Program (CHE-8204994) and the Monsanto Fund.

Supplementary Material Available: Tables of crystal data and conditions for intensity data collection, positional parameters, general temperature factor expressions, bond distances and angles, torsion angles, and observed and calculated structure factors (63 pages). Ordering information is given on any current masthead page.

Additions and Corrections

I. M. T. Davidson,* A. Fenton, S. Ijadi-Maghsoodi, R. J. Scampton, N. Auner, J. Grobe, N. Tillman, and T. J. Barton*: Kinetics and Mechanism of Pyrolysis of Hydridosilacyclobutanes. 1984, *3*, 1593.

In Table II, compounds 4 and 17 have been switched in column 2, thus affecting the values in the last four columns. Also in Table II, the k_{800K} value for total decomposition of 1 is 0.037 s^{-1}.

Book Reviews

Organometallic Chemistry of Rhodium and Iridium. By R. S. Dickson. Academic Press, New York. 1983. vi + 421 pages. $85.00.

This volume is organized in a straightforward way that makes it relatively easy to find any particular subject. The table of contents lists several section headings under each chapter. The chapter titles are as follows: (1) The General Chemistry of Rhodium and Iridium—A Brief Survey [9 pp], (2) Carbonyls and Their Substitution Products [32 pp], (3) Carbonyl-Halide and -Hydride Complexes [85 pp], (4) Pseudo Carbonyls—Complexes with M–CS, M–PF_3, M–CNR, M–NO, and M–N_2R Bonds [33 pp], (5) π-Organo Rhodium and Iridium Complexes [89 pp], (6) π-Complexes Formed from Alkynes [24 pp], and (7) σ-Alkyl, -Aryl and Related Complexes [60 pp]. The text is followed by a list of 2014 references organized alphabetically by the first author's surname. Coverage is stated to be comprehensive through the end of 1978, with key references from 1979 also included. However, an annotated addendum of "Key References from the Recent Literature" extends coverage into 1982. A reasonably detailed subject index [11 pp] is included also. In general discussion of a particular topic focuses first on rhodium then on iridium. The author's style is clear and direct, resulting in technical prose that is still highly readable. The print quality of both text and figures is very good.

The subject matter of this book is also covered in the recently published multivolume set "Comprehensive Organometallic Chemistry". In the latter treatise rhodium and iridium are presented in separate chapters with quite different styles. The rhodium chapter is excellent, current through 1980, and is packed with numerous figures and tables, but the iridium chapter is not as up-to-date or well organized. Thus, a very strong point of the present volume is its discussion of the rhodium and iridium chemistry in tandem. This not only generally follows the historical development but also provides thought-provoking contrasts as well as parallels. Given the cost of this volume and the nature of this rapidly developing area, the book will be relegated to the library shelves. However, it should be available to anyone interested in rhodium or iridium organometallic chemistry.

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Organic Reactions. Volume 32. W. G. Dauben, Editor in Chief. Wiley, New York. 1984. vi + 533 pages. $54.95.

Volume 32 of *Organic Reactions* contains two reviews, one on a mature topic, i.e., *the Intramolecular Diels–Alder Reaction*, and the other on a rapidly growing topic, i.e., *Syntheses Using Alkyne-Derived Alkenyl- and Alkynylaluminum Compounds.*

The first chapter by E. Ciganek (Du Pont) is a 374-page review presenting a 95-page discussion of various aspects of the intramolecular Diels–Alder reaction including (i) mechanism, (ii) effect of solvents, pressure, and catalysts, (iii) regio- and diastereoselectivities and syn/anti selectivities, (iv) scope and limitations with respect to the chain, dienophile, and diene moieties, and (v) synthetic utility.

A brief discussion of experimental conditions (3 pages) with one general and five specific procedures, which could have been more extensive and detailed, is followed by an extensive tabular survey (255 pages) consisting of 28 tables. They are arranged according to diene types, chain length, point of attachment of the chain, and dienophiles. The highly systematic organization of the review makes retrieval of the desired information an easy and pleasant task.

The reference section contains some 750 references. The author claims that the literature of the thermal intramolecular Diels–Alder reaction is comprehensively covered through 1981. In addition, a large number of papers publised in 1982 and 1983 are included.

Except for a few aspects, such as hetero Diels–Alder reaction, the reviewed field appears to be very mature. Judging from the rate of publication in recent years, however, its application to the synthesis of natural products and other organic compounds will continue to flourish in the future. In this sense, publication of this review at this time is a very timely one.

The second chapter (143 pages) is written in an authoritative manner by one of the pioneers of the field, G. Zweifel, and one