rotation about these Si–C single bonds should be quite small. Figure 1 shows that the predicted Si=C bond distance, 1.692 Å, falls far outside the range 1.83 ± 0.04 Å provided by the experimental electron-diffraction study.[1] The predicted Si–C single bond distance, 1.873 Å, is also shorter than experiment, 1.91 ± 0.02 Å, but in this case the disagreement is much less severe. None of the other geometrical parameters of DMSE were determined by MGM,[1] but the predicted theoretical values are all quite consistent with chemical intuition.[6] Furthermore, a steadily increasing body of comparisons[7,8] between theory and experiment would suggest a typical reliability of ± 0.01 Å for bond distances predicted at the DZ + d SCF level of theory.

For an assessment of the relationship between the structures of DMSE and the parent silaethylene, the latter equilibrium geometry was theoretically determined in a manner precisely the same as that described above for DMSE. This DZ + d SCF structure for the parent is illustrated in the middle of Figure 1. Figure 1 shows that at the DZ + d SCF level of theory, the Si=C bond distances of $H_2Si=CH_2$ and $(CH_3)_2Si=CH_2$ are *identical* (*1.692 Å*) *to within one-thousandth of an angstrom.* This would certainly appear to dispense with the possibility, suggested by MGM,[1] that the Si=C distance is significantly longer in DMSE.

The only remaining satisfactory explanation of the experimental DMSE geometry is that the DZ + d SCF level of theory systematically predicts Si=C distances much too short. This possibility has been examined by explicitly determining the structure of $H_2Si=CH_2$ using highly correlated[9] wave functions. Using the DZ + d basis set, configuration interaction (CI) was carried out including all single and double excitations relative to the Hartree–Fock reference configuration. With the six core orbitals [C(1s), Si(1s,2s,2p$_x$,2p$_y$,2p$_z$)] constrained to be doubly occupied in all configurations, this approach yields a total 6920 $^1A_1$ configurations.

The DZ + d CI structure of silaethylene shown at the bottom of Figure 2 demonstrates clearly that electron correlation has little effect on the predicted Si=C bond distance. The theoretical distance is 1.705 Å, or only 0.013 Å longer than the analogous SCF result. For the above-discussed comparison of the silaethylene and DMSE structures, one anticipates that the DMSE Si=C bond distance will also be ~1.70 Å.

On the basis of previous experience,[7,8] we suggest that the exact (unknown) Si=C bond distance r_e for the unsubstituted silaethylene is 1.705 ± 0.03 Å. To our thinking this prediction causes serious doubt upon the assumptions made by MGM[1] in extracting the Si=C distance in DMSE from the reported electron-diffraction data.[10]

It should be noted that theoretical geometry predictions for molecules containing the second-row atoms Al, Si, P, S, and Cl have been much less thoroughly calibrated then those for hydrocarbons and other first-row molecules.[7-9] However, the most complete comparison, that of Collins, Schleyer, Binkley, and Pople,[11] suggests that even without polarization functions and CI, a double-zeta basis set is unlikely to yield bond distance errors greater than 0.1 Å. Furthermore, for thioformaldehyde (isoelectronic with silaethylene), our DZ basis set yields a C=S bond distance of 1.637 Å,[12] in reasonable agreement with experiment,[13]

1.611 Å. For the same molecule, with a DZ basis set augmented by sulfur d functions, Flood and boggs[14] predicted $r_e(C=S) =$ 1.600 Å. Therefore it appears extremely unlikely that the level of theory employed here results in a large error in the C=Si bond distance of DMSE.

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Metal Vapor Microsolution Optical Spectroscopy

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The synthetic utility of transition-metal vapors for the production of organometallic materials is now well recognized,[1] and experimental methodologies for combining metal vapor and ligands are widely documented.[2] In the earliest experiments a cocondensation procedure was adopted in which both reagents, under low-pressure conditions, were simultaneously deposited onto a cooled (static or rotary) surface held at cryogenic temperatures (usually 77 K for macropreparative[3] and 4.2–20 K for matrix spectroscopic experiments[4]).

In an effort to surmount the sampling problems associated with involatile or temperature-sensitive ligands, solid-state reactions, condensed-phase inhomogeneities, uncertainties in melt-down chemistry, and general handling of products, the metal vapor-rotary solution reactor was developed.[5] The synthetic versatility of this kind of device has been subsequently demonstrated in a variety of solution-phase organometallic preparations[6] and is ideally suited for combining metal vapors with liquid polymers[7] and

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(10) One referee suggested that ground-state silaethylene could conceivably be pyramidalized about the Si atom, as is the case for the lowest triplet state.[4] Such pyramidalized geometries would be expected to have significant diradical character and a longer Si–C bond distance. Our subsequent theoretical consideration of such pyramidalized structures showed them to have consistently higher total energies than the planar equilibrium geometry at the bottom of Figure 1. Details are available from the authors.
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2454 *J. Am. Chem. Soc., Vol. 103, No. 9, 1981*

Communications to the Editor

oligomers.[8] The use of low-vapor pressure reagents of the polymer and oligomer type led to the development of ambient temperature metal vapor synthesis of organometal liquid polymers[7-9] and liquid polymer supported metal clusters.[10]

To spectroscopically probe the reactive encounters that ensue in metal vapor–liquid polymer rotary reactor experiments, the fluid matrix technique was developed.[9,10] By depositing metal vapors into a thin film of a liquid polymer or oligomer adhering to an optical window of a conventional matrix apparatus, UV–visible, IR, Raman, ESR, SIMS, and EXAFS spectra can be recorded under a range of experimental conditions.[11] Studies of this type have allowed a quantification of the diffusion/complexation/ agglomeration processes of metal atoms deposited into liquid polymeric and oligomeric supports.

In this communication we wish to report on a metal vapor microsolution spectroscopic technique which provides an in situ monitor of the fate of metal atoms deposited into cryogenic solutions and therefore a means of quantifying the chemical events that occur in a macroscale metal vapor–rotary solution syntheis. The viability and scope of the method will be demonstrated with a range of examples, some drawn from the recent literature and others being novel and relating to our own research interests.

The prototype system used to demonstrate the feasibility of metal vapor–solution synthesis involved the reaction of iron vapor—with approximately 5% COD in MCH (where COD ≡ cycloocta-1,5-diene, MCH ≡ methylcyclohexane) in a rotary reactor at about 150 K.[5] By analogy with $(COD)_2Ni$ and from its reaction chemistry with other ligands the product was suggested to be $(COD)_2Fe$.[5,12] Ready decomposition of the compound to metallic iron prevented an unambiguous structural assignment by NMR, ESR, or magnetic methods to either a diamagnetic square-planar or a paramagnetic pseudotetrahedral arrangement of the four olefinic bonds about the iron.

In our metal vapor microsolution experiments, a thin 10% COD/MCH liquid film was prepared on a horizontal optical window held at 140 K by a Displex closed-cycle helium refrigerator under dynamic vacuum conditions. In the liquid temperature range 140–170 K, COD/MCH solutions can be retained in vacuo without any appreciable spectroscopic change for a period of several hours. This is quite adequate for the duration of most metal vapor microsolution spectroscopy experiments. When a furnace arrangement[13] and mass monitor[14] similar to those described in our earlier matrix isolation experiments were used, iron vapor was quantitatively deposited into the 140-K COD/MCH solution film. Figure 1A,B shows typical optical spectroscopic traces before and after iron vapor had been reacted with COD/MCH solutions. For comparison, the microsolution optical data for Co and Ni depositions are shown in Figure 1C,D. The optical data for Ni/COD/MCH are similar to that reported for $(COD)_2Ni$ (main absorption, 274 nm) prepared by conventional means.[15] Interestingly, 77-K Fe/COD/MCH codepositions produce only $Fe_{colloid}$ as seen by the characteristic very broad optical resonance at around 300 nm. This is in agreement with earlier observations that $(COD)_2Fe$ cannot be formed under 77-K cocondensation conditions.[16] In Figure 1, it is significant to note
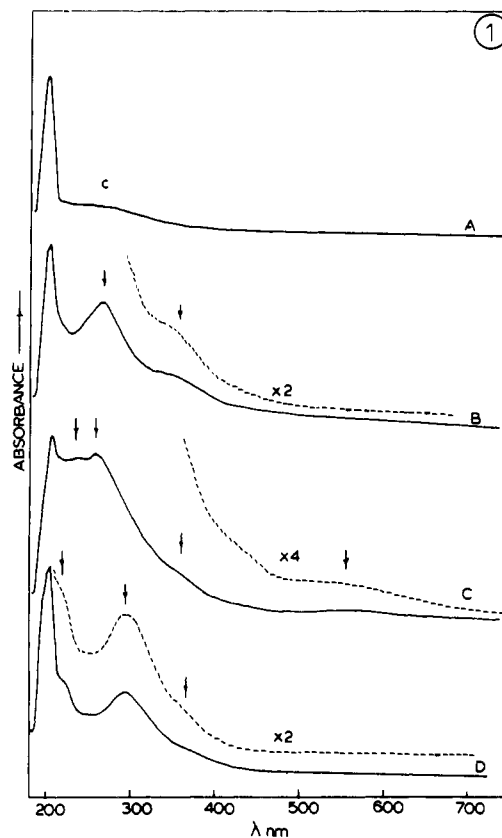

Figure 1. Optical spectra of a (A) 10% COD/MCH solution film deposited at 140 K followed by deposition of (B) iron, (C) cobalt, and (D) nickel vapor (arrows indicate $(COD)_2M$ product absorptions and c is a weak COD absorption).

the irregular spectral shifts of the main UV MLCT bands of $(COD)_2M$ on passing from Fe to Co to Ni, the presence of observable LMCT bands in the visible region only for the Co complex,[19] and the splitting of the most intense UV band of the Fe complex (267 nm) into two bands for the Co (257, 230 nm) and Ni (285, 220 nm) complexes, with increasing splitting energies on passing from Fe to Co to Ni. These data strongly suggest that $(COD)_2Fe$ and $(COD)_2Ni$ are unlikely to be isostructural. This is not surprising in view of the X-ray evidence for d^{10} pseudotetrahedral $(COD)_2Ni^{17}$ and NMR evidence[18] for the d^8 square-planar $(COD)_2Rh^+$ complex. Detailed IR, ESR, and electronic spectral studies are presently under way with these and other $(COD)_2M$ complexes.

The iron vapor–arene reaction[20] is another system that has evoked considerable interest because of the high lability of the proposed bis(arene)iron complex to ligand substitution reactions.[21-23] Whether the system exists as the 20-electron (η^6-η^6), 18-electron (η^4-η^6), or 16-electron (η^4-η^4) bis(arene) complex is still uncertain, although the iron vapor mesitylene system after warmup to room temperature has been shown to give the hydrogen-transfer product,[22] (η^6-mesitylene)(η^4-1,3,5-trimethylcyclohexa-1,3-diene)iron. A titration by iron vapor of a 10% toluene/MCH 150-K microsolution is shown in Figure 2A. Three absorptions (labeled a), maintaining the same relative intensities, grow in at 300, 355, and 436 nm. These spectra should be con-

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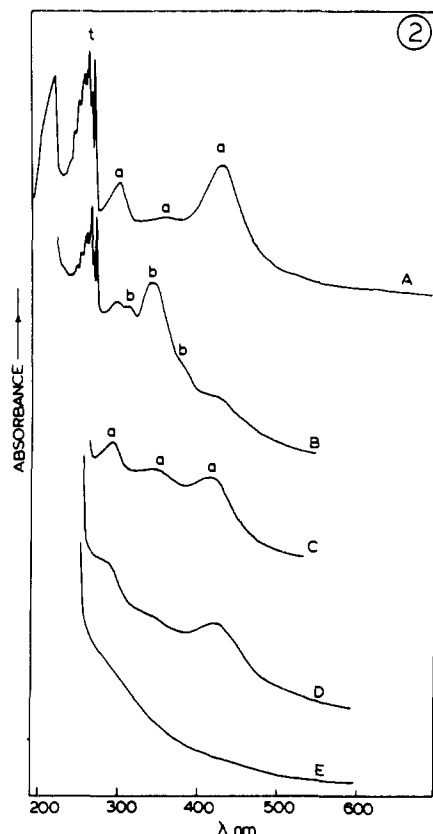(23) H. F. Efner, D. E. Tevault, W. B. Fox, and R. R. Smardzewski, *J. Organomet. Chem.*, **146**, 45 (1978).

Figure 2. Optical spectra obtained on (A) depositing iron vapor into a 10% toluene/MCH solution film at 150 K, (B) codepositing iron vapor and 10% toluene/MCH mixtures at 77 K, (C) melting the sample shown in (B) at 140 K, (D) depositing iron vapor into a poly(phenylmethyl)-siloxane DC510 film at 230 K, and (E) warming the sample shown in (D) to 270 K (a and b refer to the high- and low-temperature forms of bis(toluene)iron; t is a toluene absorption).

Figure 3. Optical spectra obtained on depositing vanadium vapor into (A) a poly(phenylmethyl)siloxane DC510 film at 250 K and (B) a 10% toluene/MCH solution film at 160 K.

Figure 4. Optical spectra obtained on depositing zirconium vapor into (A) a 10% toluene/MCH solution film at 140 K followed by the addition of either (B) N_2, (C) CO, (D) PEt_3, and (E) depositing zirconium vapor into a poly(phenylmethyl)siloxane DC510 film at 270 K.

trasted with a 10% toluene/MCH 77-K matrix cocondensation experiment shown in Figure 2B. New absorptions labeled (b) at 310, 340, and 378 nm can be seen to coexist with those labeled (a), the former decaying to zero on melting the matrix at 140–160 K (Figure 2C), with the concomitant appearance of species (a). These data reveal the presence of a low- (b) and high- (a) temperature complex in the Fe/toluene system. Species (a) shows a similar optical spectrum to that observed in the Fe/mesitylene/MCH microsolution (304, 403, and 433 nm) also prepared and observed at 150 K. These iron data differ from those of the 16,17,18-electron bis(arene)metal complexes of Ti, V, and Cr in that they display very intense UV MLCT absorptions around 430 nm, whereas the Ti, V, and Cr group show their most intense absorption in the range 320–360 nm.[8–10] One can tentatively associate the 430-nm band with MLCT from the iron to the diene π^* levels. The optical data for iron vapor deposited into a poly(phenylmethyl)siloxane (DC510) liquid film at 230 K (Figure 2D) show rather clear evidence for polymer-supported bis(arene)iron in the proposed high-temperature form (a). This species decomposes to colloidal iron around 0 °C (Figure 2E) in accord with previous work on the iron/arene system.[7,8] Collecting together the available data one can tentatively associate species (a) with (η^4-toluene)(η^6-toluene)iron and species (b) with either mono- or bis(η^6-toluene)iron or bis(η^4-toluene)iron, respectively. This system is under investigation.

Remaining with metal vapor–toluene microsolution reactions and remembering that vanadium atoms deposited into DC510 at 250 K yield both polymer-supported bis(arene)vanadium[7,8] and polymer-stabilized divanadium clusters[9,10] (characterized by optical absorptions at 324 and 453 nm, respectively, Figure 3A), one finds that similar species can be generated at 160 K in 10% toluene/MCH solutions as shown in Figure 3B. The absorption at 450 nm grows in with respect to that at 333 nm with increasing
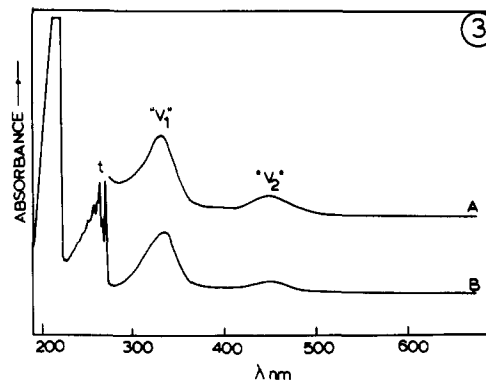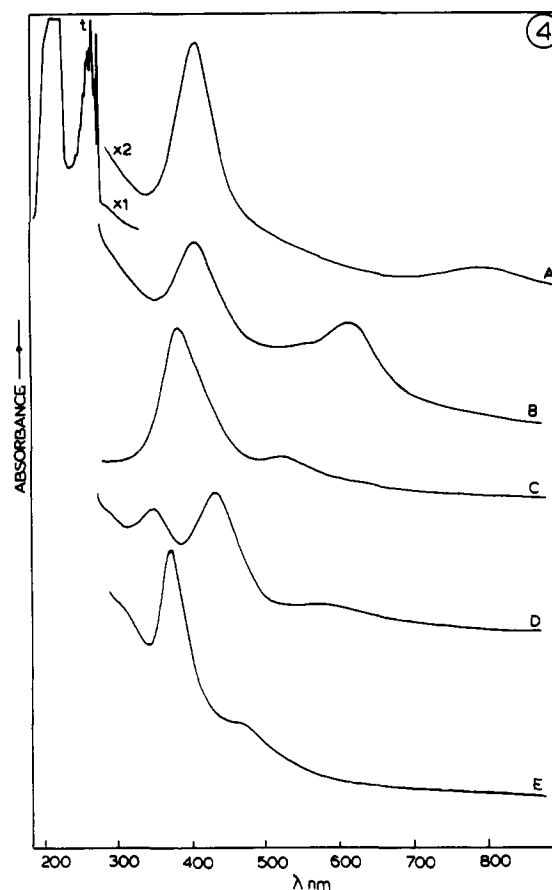
vanadium atom concentration. This behavior parallels that observed in DC510, as well as in phenyl substituted oligoethers,[24] and can be associated with a binary toluene–vanadium cluster species $(C_6H_5CH_3)_nV_2$. Work is under way to isolate and thoroughly characterize this divanadium species.

A final microsolution example concerns the zirconium–toluene reaction. Earlier work has shown that $(C_6H_5CH_3)_2Zr(PMe_3)$ can be synthesized by the reaction of zirconium vapor/toluene 77-K cocondensates with trimethylphosphine.[25] The existence of bis(toluene)zirconium(0) in the 77-K cocondensates was inferred but not proven from these studies.[25] Optical spectroscopic monitoring of Zr vapor depositions into 10% toluene/MCH 140-K

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microsolutions result in the evoluton of a single species absorbing strongly at 400 and 790 nm (Figure 4A). (These data should be contrasted with those for Zr/toluene/Ar 12-K matrix cocondensations, which show a major absorption at 360 nm and which is believed to be associated with the authentic $(\eta^6\text{-}C_6H_5CH_3)_2Zr^{26}$ complex). In situ addition of PEt_3 to this solution at 140 K causes a rapid spectral transformation (Figure 4D) with new bands at 350 and 432 nm believed to be characteristic of $(\eta^6\text{-}C_6H_5CH_3)_2Zr(PEt_3)$. The remarkable reactivity of these Zr/toluene/MCH 140-K solutions can be appreciated from the spectral alterations induced by in situ addition of CO(383, 612 nm), N_2(400, 610 nm) (see for example, Figure 4C,B) and THF (410, 840 nm). The resemblance of these optical data to that of the product of depositing Zr vapor with DC510 at 250 K, 375, 470 nm (Figure 4E) is noteworthy. Of interest also is the observation that the species formed on reacting Zr/toluene/MCH 140-K solutions with THF will not react further with CO but is converted by PEt_3 to the postulated $(\eta^6\text{-}C_6H_5CH_3)_2Zr(PEt_3)$ complex, as evidenced by the growth of bands at 350 and 432 nm (vide supra). The Zr/toluene microsolution optical data and ligand displacement information can be tentatively rationalized in terms of a 16-electron bis(toluene)zirconium(0) complex, in which the vacant coordination site may be occupied by a weakly bonding, possibly η^2-toluene, ligand. Work is also continuing on this fascinating system.

The aforementioned examples rather convincingly demonstrate the feasibility of spectroscopically probing the progress of metal vapor–solution reactions and subsequent in situ ligand additions by using optical spectroscopy. An extension to other forms of spectroscopy is straightforward. Clearly the method holds great potential for studying the spectroscopy and chemistry of organometallic reactive intermediates in solution and for optimizing the yields and elucidating the thermal stabilities of specific products in macroscale metal vapor–solution syntheses.

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Ru5(CO)13(C≡CPh)(PPh2): A Square-Pyramidal Ruthenium Cluster with a Single μ4-Bound Acetylide

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The potential utility of polynuclear transition-metal clusters in homogeneous catalysis has spurred efforts to investigate the chemistry of unsaturated molecules bound in multisite fashion to several metal atoms.[1] In the specific context of CO hydrogenation it has been suggested that μ_2-η^2 or μ_3-η^2 bonding of CO may be important in CO activation, particularly to C–O bond cleavage, generating carbidic carbon atoms.[2] Although there is recent evidence that cluster-bound carbides show unique reactivity,[3,4] knowledge of the chemical behavior of cluster carbides,

Figure 1. Polyhedral stereochemistry of Ru5(CO)13(C≡CPh)(PPh2). Skeletal Ru–Ru bond lengths are shown (inset). Other important bond lengths and angles not mentioned in the text are Ru(4)–P 2.294 (2), Ru(5)–P 2.278 (2) Å; ∠Ru(4)–C(14)–Ru(5) 79.7 (0), ∠Ru(1)–C(14)–Ru(2) 79.1 (0), ∠C(14)–C(15)–Ph 141.4 (4)°.

or their relatives the cluster-bound acetylides, is generally lacking.

In exploring the patterns of reactivity for sideways-bound acetylides, we have synthesised and characterized a unique square-pyramidal ruthenium carbonyl cluster in which the acetylide is bonded in a hithertofore unknown μ_4-η^2 fashion. No pentanuclear carbonyl clusters of ruthenium have yet been structurally characterized, and, indeed, this stereochemistry is relatively rare for other metals.[5,6] Within the iron subgroup only $Fe_5(CO)_{15}C$,[7] $Fe_5N(CO)_{14}H$,[8] and $Os_5(CO)_{15}(POMe)$,[9] all with square-pyramidal metal skeletons, have been structurally characterized.[10] The molecule $Ru_5(CO)_{13}$ (C≡CPh)(PPh2) is a member of the interesting acetylide series $Ru_2(CO)_6(\mu_2$-η^2-$C_2R)(PPh_2)$, $Ru_3(CO)_9(\mu_3$-η^2-$C_2R)(PPh_2)$, $Ru_3(CO)_6(\mu_2$-$CO)_2$-$(\mu_3$-η^2-$C_2R)(PPh_2)$ (R = Ph, i-Pr, t-Bu), and $Ru_5(CO)_{13}(\mu_4$-η^2-$C_2R)(PPh_2)(R=Ph)$.[11]

The pentanuclear cluster is generated thermally. Heating the monosubstituted ruthenium cluster $Ru_3(CO)_{11}(PPh_2C≡CPh)$ in heptane at 70 °C for 8 h results in fragmentation of the starting material to give predominantly the dinuclear carbonyl acetylide $Ru_2(CO)_6(C≡CPh)(PPh_2)$,[11] a hexanuclear product, as yet uncharacterized, and $Ru_5(CO)_{13}(C≡CPh)(PPh_2)$ which precipitates from the reaction mixture in 30% yield on concentration in vacuo.[12] Infrared studies[13] confirmed the presence of only terminal carbonyl groups and a ^{31}P NMR spectrum suggested a single phosphido

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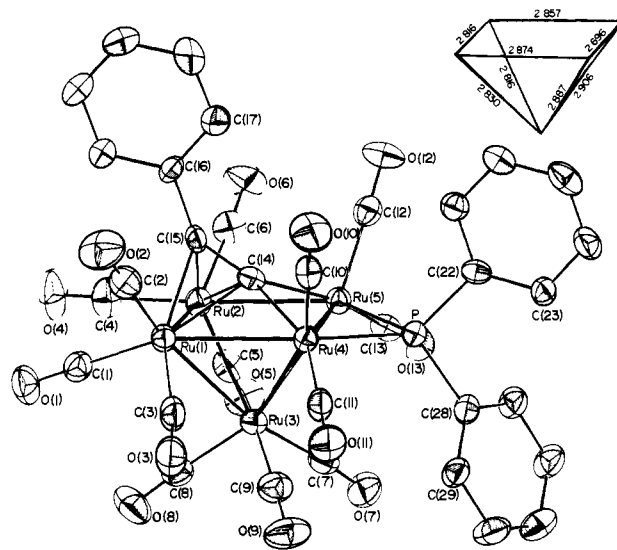(4) Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4541–4542.

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(12) The pentanuclear cluster was separated from traces of $Ru_3(CO)_{12}$ by dissolution in benzene, followed by chromatography through a short (12 cm) Florisil column. Blue-black crystals were obtained from heptane–benzene solutions (yield 30%), mp 214–216 °C. Anal. Calcd: C, 34.29; H, 1.31; P, 2.68. Found: C, 34.62; H, 1.35; P. 2.68.

(13) IR ν(CO) (C_6H_{12}) 2076 m, 2043 vs, 2024 s, 2014 m, 2000 w cm^{-1}; ^{31}P NMR (C_6D_6) δ (with respect to 85% H_3PO_4) +253.