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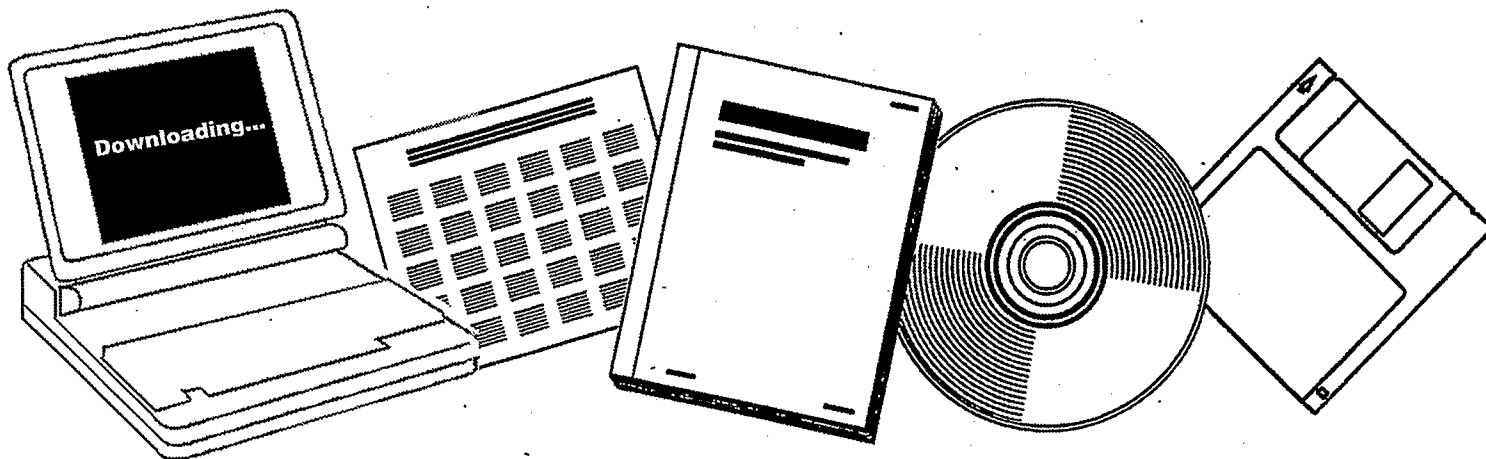
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**MECHANISTIC STUDIES OF CARBON MONOXIDE
REDUCTION: PROGRESS REPORT, JANUARY 1,
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PARK. DEPT. OF CHEMISTRY

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MECHANISTIC STUDIES OF CARBON MONOXIDE
REDUCTION

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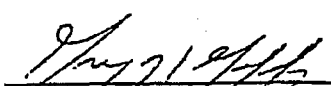
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Publications Resulting from this DOE Grant

(*No's 12-15 have been added since the 8/86 report)

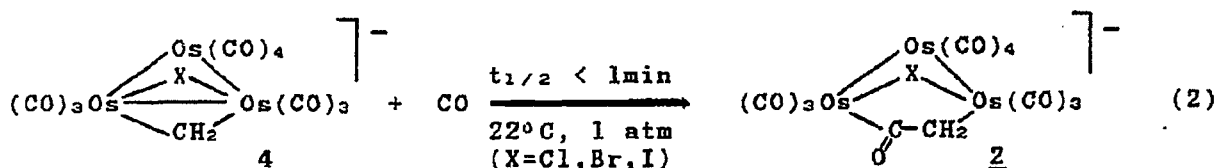
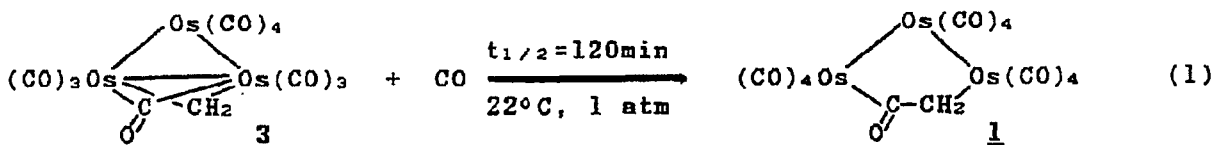
- Williams, G. D.; Geoffroy, G. L., Whittle, R.R., Rheingold, A. L., "Formyl, Acyl, and Carbene Derivatives of $\text{Fe}_3(\mu_3\text{-EPh})_2(\text{CO})_9$ (E=N,P). Unique Examples of Carbene-Nitrene and Carbene-Phosphinidene Coupling", J. Am. Chem. Soc. **1985**, 107, 729.
- Morrison, E. D.; Geoffroy, G. L. "Halide-Promoted Insertion of Carbon Monoxide into Osmium- μ -Methylene Bonds in Triosmium Clusters", J. Am. Chem Soc. **1985**, 107, 3541.
- Morrison, E. D.; Whittle, R. R.; Geoffroy, G. L.; Rheingold, A. L. "Fifty Electron $[\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)(\mu\text{-X})]^-$ Clusters Derived from Reaction of $\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2)$ with $[(\text{PPh}_3)_2\text{N}]\text{X}$ Salts. Structural Characterization of the $\text{X} = \text{NCO}$ and I Derivatives. Organometallics, **1985**, 4, 1413.

4. Morrison, E. D.; Bassner, S. L.; Geoffroy, G. L. "Synthesis of $\text{Os}_3(\text{CO})_{10}(\text{CH}_3)(\mu\text{-I})$ with an η^1 -Methyl Ligand and Its Insertion of CO to give Acetyl Derivatives", Organometallics, **1986**, 5, 408.
5. Targos, T. S.; Geoffroy, G. L.; Rheingold, A. L. "Synthesis and Molecular Structure of the μ -Acetyl Complex $\text{Cp}(\text{CO})_2\text{Mo}(\mu\text{-O=CCH}_3)(\mu\text{-PPh}_2)\text{FeCp}(\text{CO})$ ", J. Organomet. Chem. **1986**, 299, 223.
6. Williams, G. D.; Geoffroy, G. L. "Reaction of $(\text{MeCp})\text{Mn}(\text{CO})_2(\text{THF})$ with PhCH_2N_3 to Yield Binuclear $(\text{MeCp})_2\text{Mn}_2(\text{CO})_3[\mu\text{-C(O)N}(\text{CH}_2\text{Ph})\text{N}_2]$, an Intermediate in the Formation of Benzyl Isocyanate", Organometallics, **1986**, 5, 894.
7. Viswanathan, N.; Morrison, E. D.; Geoffroy, G. L.; Geib, S. J.; Rheingold, A. L. "Insertion of SnCl_2 into an Os-Os Bond of $\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2)$ to Give the Planar Cluster $\text{Os}_3\text{SnCl}_2(\text{CO})_{11}(\mu\text{-CH}_2)$ with a Pentacoordinate Tin Atom", Inorg. Chem., **1986**, 25, 3100.
8. Williams, G. D.; Lieszkovszky, M.-C.; Mirkin, C. A.; Geoffroy, G. L.; Rheingold, A. L. "Addition of the Os-CH₂ Bond in $\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2)$ to $\text{Pt}(\text{PPh}_3)_2$ to Give the Spiked Triangular Cluster $\text{Os}_3\text{Pt}(\mu\text{-CH}_2)(\text{CO})_{11}(\text{PPh}_3)_2$. An NMR Investigation of the Fluxional Properties of $\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2)$ " Organometallics, **1986**, 5, 2228.
9. Bassner, S. L.; Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. "Conversion of the μ -Ketene Ligand in $[\text{PPN}][\text{Os}_3(\text{CO})_{10}(\mu\text{-I})(\mu\text{-CH}_2\text{CO})]$ into Enolate, Acyl, and Vinyl Ligands" J. Am. Chem. Soc., **1986**, 108, 5358.
10. Williams, G. D.; Whittle, R. R.; Geoffroy, G. L.; Rheingold, A. L. "Formation of Imidates, Amides, Amines, Carbamates, and Ureas from the μ_3 -NPh Ligands of $\text{Fe}_3(\mu_3\text{-NPh})_2(\text{CO})_9$ " J. Am. Chem. Soc., in press.
11. Bassner, S. L.; Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. "Conversion of the μ -Ketene Ligand in $[\text{PPN}][\text{Os}_3(\text{CO})_{10}(\mu\text{-I})(\mu\text{-CH}_2\text{CO})]$ into Enolate, Acyl, and Vinyl Ligands. Crystal Structure of the Enolate Cluster $[\text{PPN}][\text{Os}_3(\text{CO})_{11}(\text{CH}_2\text{C(O)OCH}_3)]$." Organometallics, in press.
- *12. Geoffroy, G. L.; Bassner, S. L. "Interaction of ketenes with Organometallic Compounds. Ketene, Ketenyl, and Ketenylidene Complexes" Adv. Organomet. Chem., in press.
- *13. Macklin, P. D.; Mirkin, C. A.; Viswanathan, N.; Williams, G. D.; Geoffroy, G. L. "Synthesis of $\text{Cp}(\text{CO})\text{CoPt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ and $\text{Cp}_2\text{Co}_2\text{Pt}(\text{PPh}_3)_2(\mu\text{-CO})_2$ from the Reaction of $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ with $[\text{CpCo}(\text{CO})]_2(\mu\text{-CH}_2)$ " J. Organomet. Chem., in press.
- *14. Han, S. H.; Geoffroy, G. L., and Rheingold, A. L. "Halide Promoted Formation and Carbonylation of μ_3 -Nitrene Ligands" J. Am. Chem. Soc., submitted for publication.
- *15. Han, S. H.; Geoffroy, G. L.; Rheingold, A. "Ru₆(CO)₁₅(μ_3 -NPh)₂: An Unusual Cluster with a Structure Having Two Fused Butterflies each Bridged by a μ_4 -NPh Ligand", in preparation.
- *16. Bassner, S. L.; Geoffroy, G. L.; Rheingold, A. "Isocyanide Induced Insertion of CO into Osmium-Methylene Bonds to Form μ -Ketene Ligands", in preparation.

Narrative

There is strong evidence that surface bound carbenes play important roles in heterogeneous synthesis gas reactions to produce hydrocarbons and oxygenated products.¹ One important reaction that such species may undergo is insertion of CO to give ketenes which have been invoked as intermediates in the production of both C₂-oxygenates and hydrocarbons.² Also, the insertion of CO into metal-carbene bonds to give ketene complexes is developing as an important step in many stoichiometric reactions of organometallic compounds³ and is now finding applications in organic synthesis.⁴

Although a few ketene complexes had been characterized at the time we began research under the present DOE grant, the chemistry of coordinated ketenes had been scarcely investigated. For example, it was not understood how the ketene coordination mode affected the reactivity of this ligand nor even what types of transformations were possible. We had previously demonstrated that the methylene ligands in clusters 3 and 4 readily insert CO to form μ -ketene ligands, eqs. 1 and 2.^{5,6}



With these results in hand, we decided to undertake a reactivity study of the ketene clusters 1 and 2 so as to define the chemistry of this important ligand. That became a major objective of the present research program. Secondary objectives were to prepare new ketene complexes with other metal ligand combinations and to further develop the chemistry of the μ -CH₂ clusters 1 and 2.

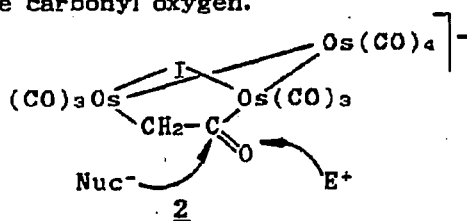
Since the μ -CH₂ \rightarrow μ -CH₂CO conversion worked so smoothly in this system, we considered the possibility of analogously inserting CO into metal-nitrene bonds to form free or coordinated isocyanates (μ_3 -NR \rightarrow μ -RNC=O). This is an important reaction because of the industrial interest in converting inexpensive

nitro-organics via carbonylation into value-added products such as isocyanates, carbamates, and ureas. Thus, a second major objective of this research program was to determine if μ_3 -NR ligands undergo such carbonylation chemistry. What we discovered is that halides exhibit a remarkable promoting effect on these carbonylation reactions, as they also did on the methylene carbonylation reactions of eqs. 1 and 2. There are a number of examples of halide promoted organometallic transformations, many of them catalytic, but relatively few are understood in any detail. In order to optimize and intelligently employ such promotion chemistry, it is essential to have a better understanding of why and how it works. Thus, we began to investigate the halide promoted μ_3 -NR \rightarrow RN=C=O conversion in detail so as to provide fundamental information for this example. Those studies are still in progress, but important advances have been made.

This report briefly summarizes our progress in all of these areas, beginning with a summary of the ketene reactivity studies. That is followed by the more recent work on the nitrene carbonylation chemistry.

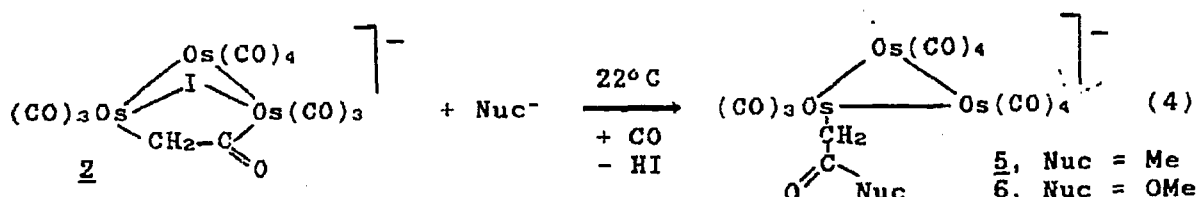
A. Transformation of Ketene Ligands into Enolate, Vinyl, and Acetyl Ligands.

In our first report of the synthesis of compound 1, we noted that it reacts with MeOH, H₂O, and H₂ to give methylacetate, acetic acid, and acetaldehyde, respectively.⁵ We have more recently focussed on the anionic ketene complex 2 and have discovered that the ketene ligand can be readily transformed into enolate, vinyl, and acetyl ligands as well as free amides.⁷ All of these studies indicate that nucleophiles attack the ketene carbonyl carbon whereas electrophiles add to the carbonyl oxygen.



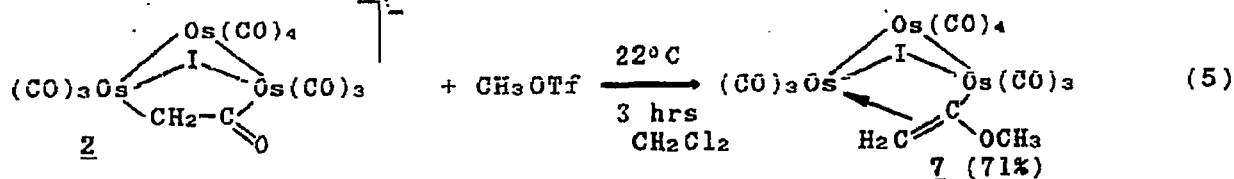
The reactions with nucleophiles parallel similar reactivity patterns with free ketene, but the electrophile reactions are different as uncoordinated ketene typically adds electrophiles to the methylene carbon.

Nucleophiles such as MeLi, NaOMe, and HOME convert the μ -ketene ligand into enolate ligands, eq. 4.

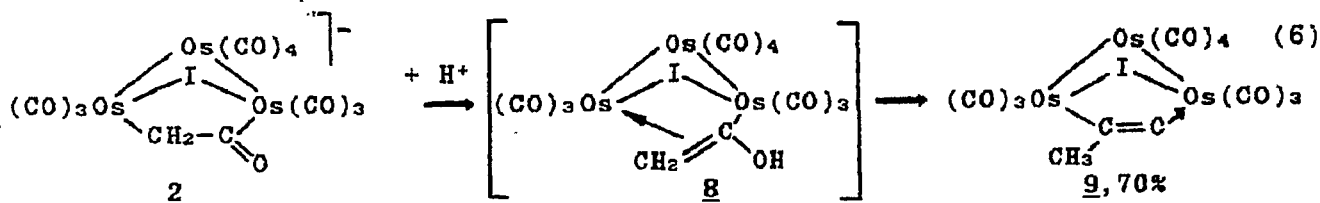


Both 5 and 6 were spectroscopically characterized, with the structure of 6 fully confirmed by an X-ray diffraction study, Figure 1.⁷ Only two other η^1 -alkyl carbonyl clusters are known,^{8,9} one of them described below, and compounds 5 and 6 thus significantly expand this relatively small family of compounds.

Electrophiles were found to add to the carbonyl oxygen of 2, as clearly illustrated by its reaction with MeOTf to give the spectroscopically and structurally characterized σ, π -vinyl cluster 7, eq. 5.⁷

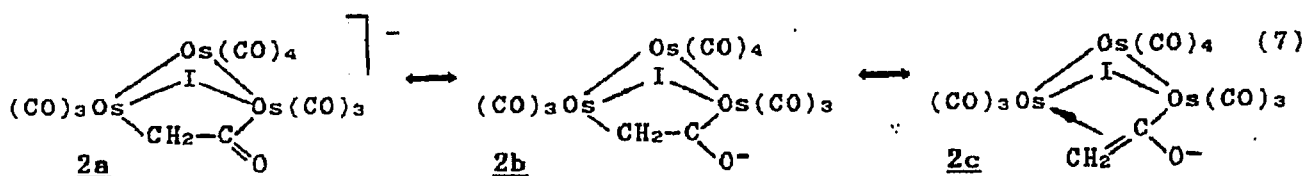


Cluster 2 also undergoes protonation at the carbonyl oxygen to first form the unstable hydroxyvinyl cluster 8.⁷ This species was spectroscopically characterized, but it rapidly undergoes keto-enol tautomerization to give the known acetyl cluster 9, eq. 6.⁷



Spectroscopic data also showed that BF_3 adds to the carbonyl oxygen to give an unstable vinyl cluster analogous to 7 and 9.⁷

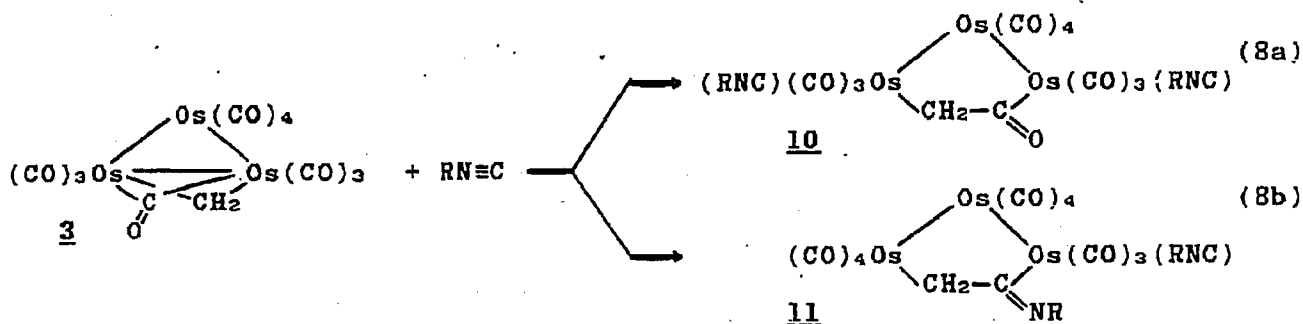
An important conclusion that can be drawn from the observed reactions of 2 with electrophiles is that oxycarbene (2b) and oxyvinyl (2c) structures are important resonance forms for this anionic cluster, eq. 7.⁷



The σ, π -vinyl resonance form is unique to an anionic ketene complex such as 2 and has no precedent in mononuclear chemistry.

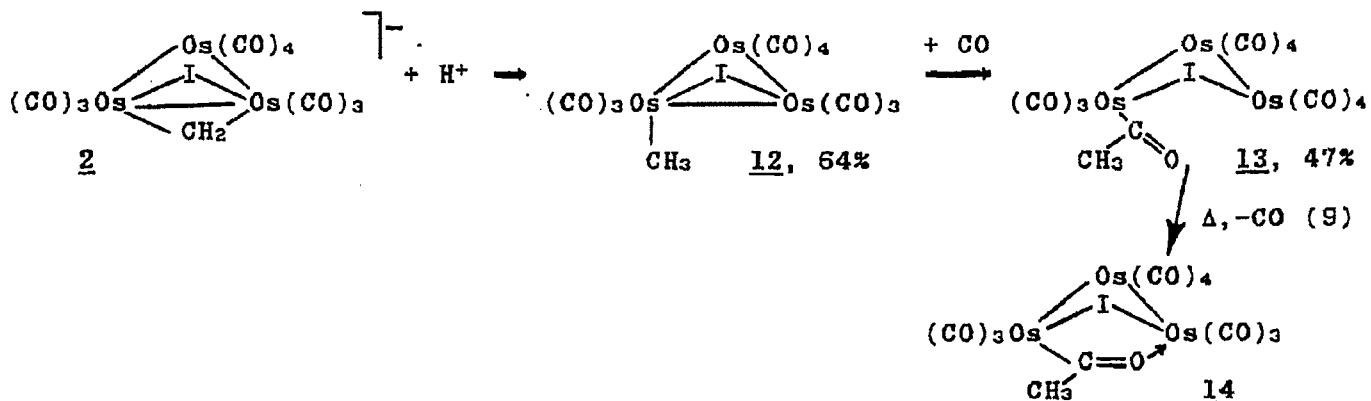
A characteristic reaction of free ketenes is their cycloaddition with olefins, alkynes, isocyanates and other unsaturated organics. We considered the possibility that the coordinated ketene ligands clusters 1 and 2 might also undergo such chemistry. Accordingly, the reactions with potential substrates such as $\text{CH}_2=\text{CH}(\text{OEt})$, $\text{PhHC}=\text{NMe}$, and $\text{MeO}_2\text{CC}=\text{CCO}_2\text{Me}$ was explored, but in no case was reaction observed. These ketene complexes also failed to give clean chemistry with $\text{BH}_3\cdot\text{THF}$, LiBHET_3 , MeI , and NaNH_2 .

B. Isocyanide Induced Ketene Formation. An interesting question concerns how isocyanides would react with the $\mu\text{-CH}_2$ clusters 2 and 3. Isocyanides are isoelectronic with CO and could either induce CO insertion to form a ketene ligand as in 10, eq. 8a, or could themselves insert to form an analogous ketenimine ligand as in 11, eq. 8b.



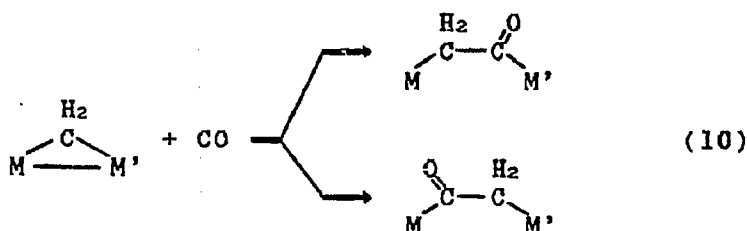
Reaction with 3 and $\text{Bu}^t\text{N}\equiv\text{C}$ was found to proceed smoothly to give only the ketene complex 10 which was spectroscopically and structurally characterized.

C. Proton Induced $\mu\text{-CH}_2$ to CH_3 Conversion. Methylene and methyl fragments are believed to be important surface intermediates in many heterogeneous catalytic reactions, and an important reaction is their transformation into one another by hydrogen addition/elimination. To model this chemistry, we protonated the anionic methylene cluster and observed its transformation into the methyl substituted cluster 12, eq. 9.⁵

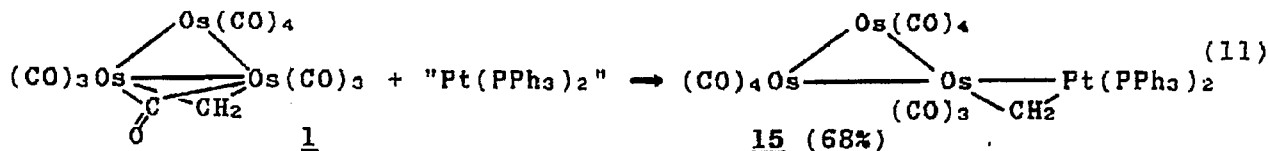


Methyl complex 12 is the only example of which we are aware of a simple alkyl substituted carbonyl cluster without an "agostic" M-H-C interaction. Like mononuclear alkyl complexes, it readily inserts CO to form a terminal acetyl cluster (13) which then loses CO to form the μ -acetyl cluster 14. This reaction had never before been modeled on a cluster compound because of the lack of a suitable alkyl cluster to study.

D. Heterobimetallic μ -Methylene and μ -Ketene Complexes. We wished to examine the CO insertion chemistry of a series of *heterometallic* μ -CH₂ complexes to determine from which metal does the insertion occur and whether or not the ketene ligand can undergo the coordination isomerism shown in eq. 10.

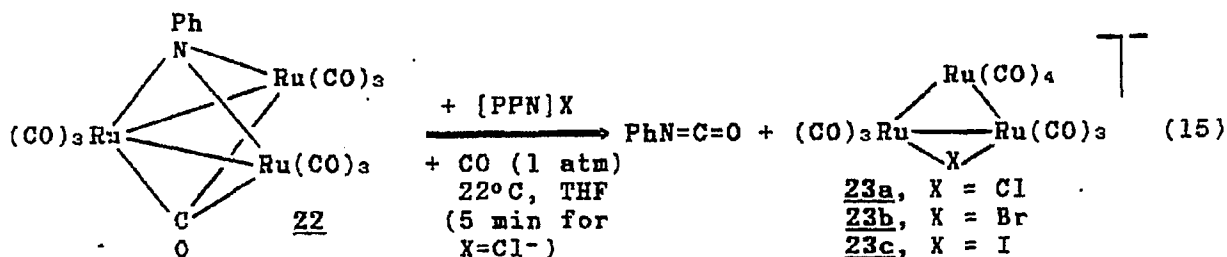


A number of heterobimetallic μ -CH₂ complexes are known, but none are known to undergo CO insertion to form μ -ketene complexes. Since Os₃(CO)₁₁(μ -CH₂), 1, readily undergoes such reaction, a heterometallic derivative of this complex would be a viable candidate to explore the issues of eq. 10. We thus treated 1 with Pt(PPh₃)₂(CH₂=CH₂) and formed the PtOs₃ cluster 15, eq. 11.¹⁰

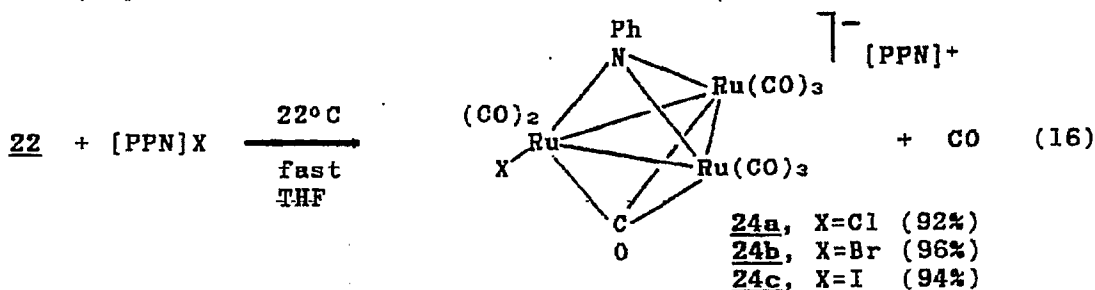


The structure of 15 is rather unusual and so it was crystallographically characterized, Figure 2. Unfortunately, 15 did not form a ketene ligand when

E. Halide Promoted Formation and Carbonylation of Nitrene Ligands. Nitrene ligands are believed important in the catalytic carbonylation of nitroaromatics to form isocyanates, carbamates, ureas, and other organics.¹⁴ Although details of the mechanisms of these carbonylation reactions are unknown, the stepwise deoxygenation process $\text{RNO}_2 \rightarrow \text{RNO} \rightarrow \text{M-NR}$ followed by carbonylation of the nitrene ligand to form RN=C=O has been often suggested. To understand these mechanisms we have used organometallic cluster compounds to model the important reaction steps. A significant finding has been the remarkable promotion of the nitrene carbonylation by halides. In the absence of halide, the nitrene cluster $\text{Ru}_3(\mu_3\text{-NPh})(\text{CO})_{10}$, **22**, has slowly (6.5hr) gives PhN=C=O and $\text{Ru}(\text{CO})_5$ under 170 atm of CO at 120°C ,¹⁵ but we observed no reaction when lower CO pressures (4 atm, 120°C , 22hr) were used.¹⁶ However addition of halide ions to **1** dramatically promotes the carbonylation such that it rapidly proceeds under extremely mild conditions, eq. 15.¹⁶



The halide substituted clusters **24** were identified as intermediates in this process and they were isolated in high yield from reactions run in the absence of CO, eq. 16.¹⁶

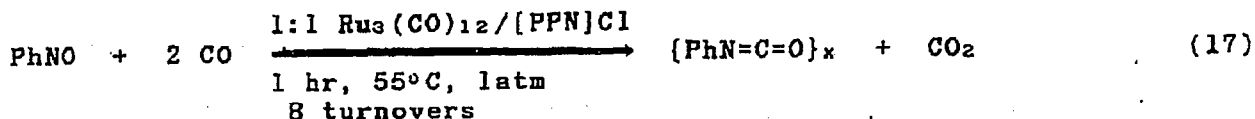


Complex **24c**, as its $[\text{Na}(18\text{-crown-6})]^+$ salt, was structurally characterized, Figure 6, and similar structures are indicated for **24a** and **24b** on the basis of IR data. The only notable structural consequence of the halide substitution was a movement of the $\mu_3\text{-CO}$ ligand closer to the iodide substituted Ru, but there was essentially no change in Ru-Ru and Ru-N distances as compared to **22**.

Clusters 24a-c were found to individually react with CO (1atm, 22°C) to give PhN=C=O and 23a-c, but with a significant halide dependence: ~t_{1/2}'s, Cl (8min) < Br (80min) < I (5hr). Although the reasons for the halide promotion of the PhN to PhN=C=O conversion are unknown, we suggest that halide may induce the insertion by assuming μ_2 or μ_3 bridging positions as the PhNCO ligand is formed and removed from the cluster. Note that the components of PhNCO donate a total of 6e⁻ in cluster 1 and occupy three coordination sites which must be filled as the isocyanate leaves.

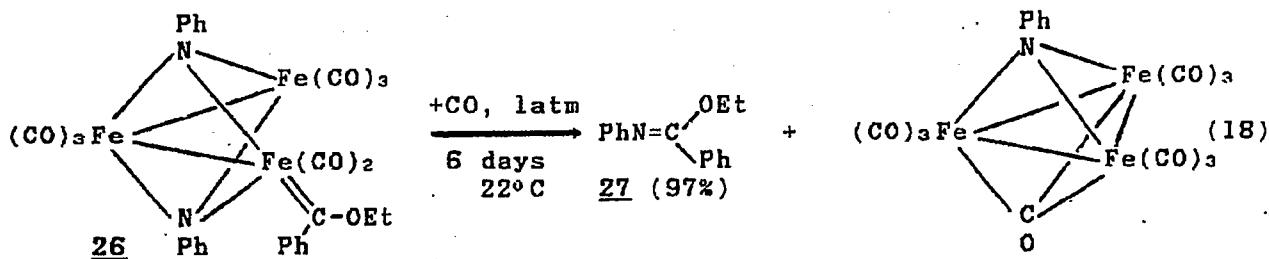
Halides also promote the formation of nitrene ligands from nitrosobenzene. The unpromoted reaction between Ru₃(CO)₁₂ and PhNO proceeds at 57°C to give 22 in 46% yield (2hr, THF).¹⁷ However, addition of PhNO to room temperature solutions of the halide clusters 23a-c results in rapid formation of 24a-c in near quantitative yield: ~t_{1/2}'s, Cl (<1min) ~ Br (<1min) < I (15min).¹⁶ We suggest that the formation of the μ_3 -NPh ligand from PhNO requires initial coordination of the nitroso reagent to a Ru atom and that the halide promotion of the PhNO to μ_3 -NPh transformation is just a simple consequence of the previously observed halide promoted ligand substitution reactions of Ru₃(CO)₁₂.¹⁸ Here the effect of halide is believed to be enhancement of the rate of CO dissociation, opening a site for the incoming ligand.¹⁸ Note that the relative halide promoting abilities of the two reactions are the same: Cl⁻ > Br⁻ > I⁻.¹⁸

Since halides promote both the formation of nitrene ligands from PhNO and the carbonylation of nitrenes to isocyanates, they should also effectively promote the catalytic carbonylation of PhNO to PhNCO under mild conditions. The results summarized in eq. 17 show this to be so, although the organic product is a mixture of phenylisocyanate dimer and trimer.¹⁶

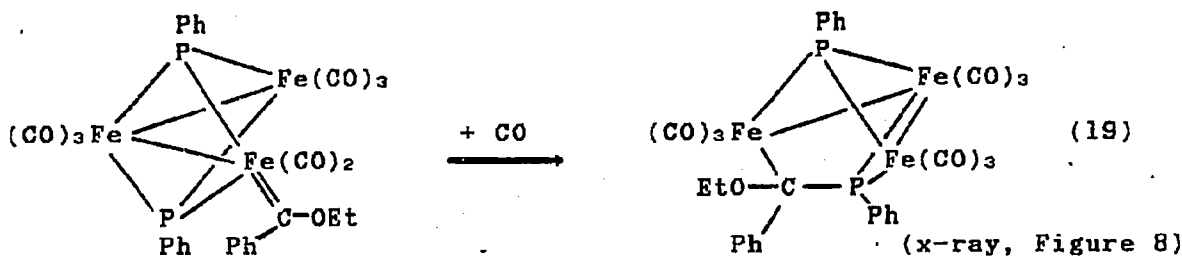


However, the catalytic activity for the PhNO to isocyanate transformation ceases after ~1 hr during which time a presently unidentified and catalytically inactive organometallic product forms.

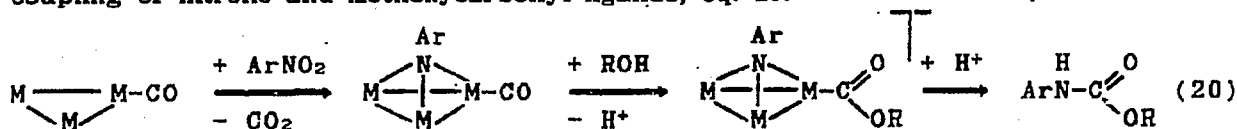
Cenini, *et al.* have previously shown that halides are effective promoters for the Ru₃(CO)₁₂ catalyzed carbonylation of PhNO₂ in the presence of ROH to



A double-labeling experiment showed that this reaction was strictly intramolecular. Similar coupling of carbene and phosphinidene ligands occurred with the analogous μ_3 -PPh cluster 28, except that the coupled ligand stayed attached to the cluster framework, eq. 19.²⁰

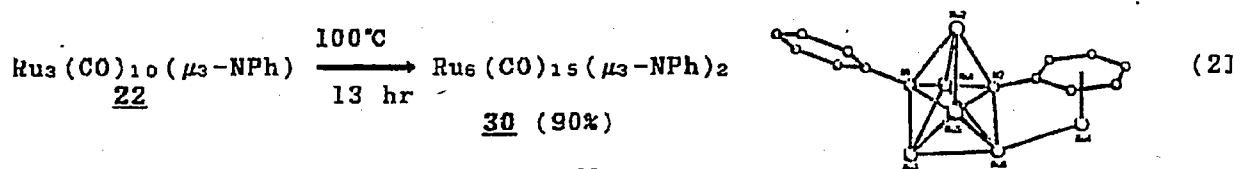


One of the questions posed in this study concerned the possibility of forming the carbamate products of catalytic nitroaromatic carbonylations via coupling of nitrene and methoxycarbonyl ligands, eq. 20.



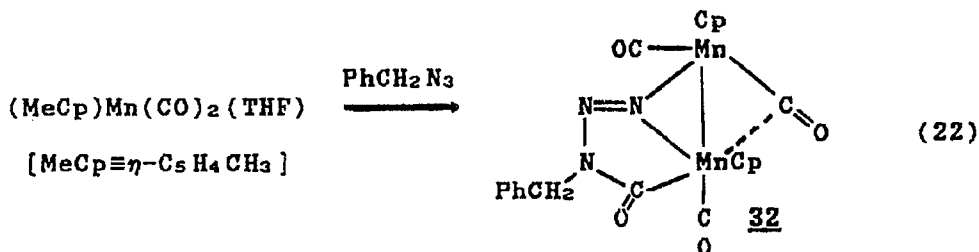
To model this reaction, the methoxycarbonyl cluster 29 in Scheme I was prepared. Indeed, this species underwent coupling of the methoxycarbonyl and nitrene ligands to form methyl N-phenylcarbamate when heated, supporting the mechanistic suggestion of eq. 20.²⁰

G. Miscellaneous Studies Related to Nitrene Clusters. In the course of attempts to carbonylate $\text{Ru}_3(\text{CO})_{10}(\mu_3\text{-NPh})$, 22, this species was heated in the absence of CO and observed to give CO loss and condensation to the unusual $\text{Ru}_6(\mu_3\text{-NPh})_2$ cluster 30, eq. 21.²¹

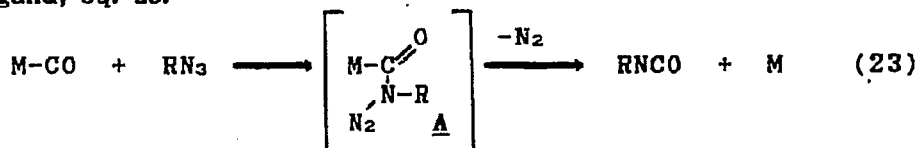


This complex was crystallographically characterized, eq. 21, and its structure is obviously unusual. Especially noteworthy are the two tetrabridging nitrene ligands and the η^6 -phenyl coordinated Ru. The mechanism by which this species forms must be complex, but analysis of its structure suggests an alternative synthesis via addition of a $\text{Ru}_3(\text{CO})_x$ fragment to the preformed bis(nitrene) cluster $\text{Ru}_3(\text{CO})_9(\mu_3\text{-NPh})_2$, **31**. Indeed, reaction between $\text{Ru}_3(\text{CO})_{12}$ and **31** gave cluster **30** in 90% yield. This latter reaction suggests that combination of **31** with other metal carbonyls may yield heteronuclear nitrene clusters of similar structures. Such reactions are currently under investigation.

Nitrene containing metal clusters are clearly in need of further study, but one problem that may limit the development of their chemistry is the paucity of compounds that contain $\mu_3\text{-NR}$ ligands and the lack of general, high yield synthetic routes to them. One potential route to $\mu_3\text{-NR}$ capped clusters is the reaction of organic azides with coordinatively-unsaturated metal carbonyls. This route has been occasionally used, but it is not general.²² We wished to extend this methodology and accordingly examined the reaction of PhCH_2N_3 with $(\text{MeCp})\text{Mn}(\text{CO})_2(\text{THF})$, anticipating the formation of a $\text{Mn}_2(\mu\text{-NR})$ cluster. However, this reaction did not produce $\mu_3\text{-NCH}_2\text{Ph}$ compounds, but rather azide-carbonyl coupling occurred to give the novel binuclear complex **32**, eq. 22.²³



The structure of this product, Figure 9, unexpectedly gave mechanistic information relevant to the azide to isocyanate conversion. The reaction of azides with CO to yield isocyanates and isocyanate derived products is catalyzed by metal complexes, but the mechanism has not been well defined. It has been suggested that it involves attack of azide on a CO ligand to give an intermediate such as **A** followed by N_2 loss and de-coordination of the RNCO ligand, eq. 23.



However, intermediates such as **A** have never been observed in mononuclear

complexes. Two examples are known with polynuclear species,²³ but the conversion of such $\mu\text{-C(O)N(R)N}_2$ ligands to the corresponding isocyanates had not been established prior to our study. We were able to show that the $\mu\text{-C(O)N(CH}_2\text{Ph)N}_2$ ligand in complex **32** readily lost N_2 to give free isocyanate when irradiated in THF solution. Mononuclear (MeCp)Mn complexes were formed in this latter reaction, and the overall sequence constitutes a cycle in which mononuclear complexes convert an azide into an isocyanate via the intermediacy of a binuclear species. This is a unique example of a reaction sequence which proceeds from a mononuclear complex to a binuclear species and then back to the mononuclear complex, where the binuclear species is a necessary component for stabilizing a reactive intermediate so that it can be subsequently transformed into the desired product.

References

1. See, for example: a) Muetterties, E.L.; Stein, J. Chem. Rev. 1979, **79**, 479. b) Bell, A. T. Catal. Rev. 1981, **23**, 203. c) Herrmann, W. A. Angew. Chem. Int. Ed. Engl. 1982, **21**, 117. d) Pettit, R.; Brady, R. C. III J. Am. Chem. Soc. 1980, **102**, 6181. e) Pettit, R.; Brady, R. C. III Ibid. 1981, **103**, 1287.
2. a) Takeuchi, A.; Katzer, J. R. J. Phys. Chem., 1982, **86**, 2438. b) Takeuchi, A.; Katzer, J. R.; Schuit, G. C. A. J. Catal., 1983, **82**, 477. c) Takeuchi, A.; Katzer, J. R.; Crecey, R. W. J. Catal., 1983, **82**, 474. c) Loggenberg, P. M.; Carlton, L.; Copperthwaite, R. G.; Hutchings, G. J. J. Chem. Soc., Chem. Commun. 1987, 541.
3. For a review on the "Interaction of Ketenes with Organometallic Complexes" see: Geoffroy, G. L.; Bassner, G. L. Adv. Organomet. Chem., in press.
4. a) Miyashita, A.; Kihara, T.; Nomura, K.; Nohira, H. Chem. Lett. 1986, 1607. b) Mitsudo, T.; Kadokura, M.; Watanabe, Y. J. Chem. Soc., Chem. Commun. 1986, 1539. c) Kadokura, M.; Mitsuda, T.; Watanabe, Y. J. Chem. Soc. Chem. Commun. 1986, 252. d) Mitsudo, T.; Kadokura, M.; Watanabe, Y. Tetrahedron Lett. 1985, **26**, 5143. e) Mitsudo, T.; Kadokura, M.; Watanabe, Y. Tetrahedron Lett. 1985, **26**, 3697.
5. Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. J. Am. Chem. Soc., 1984, **106**, 4783.
6. Morrison, E. D.; Geoffroy, G. L. J. Am. Chem. Soc. 1985, **107**, 3541.
7. a) Bassner, S. L.; Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. J. Am. Chem. Soc., 1986, **108**, 5358. b) ibid., Organometallics, in press.
8. Morrison, E. D.; Bassner, S. L.; Geoffroy, G. L. Organometallics, 1986, **5**, 408.
9. Zuffa, J. L.; Gladfelter, W. L., J. Am. Chem. Soc. 1986, **108**, 4669.

10. Williams, G. D.; Lieszkovszky, M.-C.; Mirkin, C. A.; Geoffroy, G. L.; Rheingold, A. L. Organometallics, 1986, 5, 2228.
11. Viswanathan, N.; Morrison, E. D.; Geoffroy, G. L.; Geib, S. J.; Rheingold, A. L. Inorg. Chem., 1986, 25, 3100.
12. Macklin, P. D.; Mirkin, C. A.; Viswanathan, N.; Williams, G. D.; Geoffroy, G. L. J. Organomet. Chem., in press.
13. Bassner, S. L.; Mercer, W.; Geoffroy, G. L. unpublished results.
14. a) Andrews, M. A.; Kaesz, H. D. J. Am. Chem. Soc. 1979, 101, 7255. b) Bhaduri, S.; Gopalkrishnan, K. S.; Clegg, W.; Jones, P. G.; Sheldrick, G. M.; Stalke, D. J. Chem. Soc., Dalton Trans. 1984, 1765. c) Bernhardt, W.; Von Schnering, C.; Vahrenkamp, R. Angew. Chem. Int. Ed. Engl. 1986, 25, 279. d) Dawoodi, Z.; Mays, J.; Henrick, K. J. Chem. Soc., Dalton Trans 1984, 433. e) Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F.; Monica, G. L. J. Chem. Soc., Chem. Commun. 1984, 1286. f) Alper, H.; Hashem, K. E. J. Am. Chem. Soc. 1981, 103, 6514. g) des Abbayes, H.; Alper, H. J. Am. Chem. Soc. 1977, 99, 98. h) L'Eplattenier, F.; Matthys, P.; Calderazzo, F. Inorg. Chem. 1970, 9, 342. i) Weigert, F. J. Org. Chem. 1973, 38, 1316. j) Braunstein, P.; Bender, R.; Kervennal, J. Organometallics, 1982, 1, 1236. k) Alper, H.; Paik, H. N. Nouveau Journal De Chemie, 1978, 2, 245. l) see also US Patents 3 576 835, 3 719 699, 3 737 445, 4 491 670, and German Patents DE 1 815 517, 2 165 355, and 1 901 202.
15. Smieja, J. A.; Gozum, J. E.; Gladfelter, W. L. Organometallics. in press.
16. Han, S. H.; Geoffroy, G. L., and Rheingold, A. L. J. Am. Chem. Soc., submitted for publication.
17. Smieja, J.; Gladfelter, W. L. Inorg. Chem. 1986, 25, 2667.
18. Lavigne, G.; Kaesz, H. D. J. Am. Chem. Soc. 1984, 106, 4647.
19. Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F.; Monica, G. L. J. Chem. Soc., Chem. Commun. 1984, 1286.
20. a) Williams, G. D.; Geoffroy, G. L.; Whittle, R.R.; Rheingold, A. L. J. Am. Chem. Soc. 1985, 107, 729. b) ibid., in press.
21. Han, S. H.; Geoffroy, G. L.; Rheingold, A., in preparation.
22. For reviews, see: a) Nugent, W. A.; Haymore, B. L. Coord. Chem. Rev. 1980, 31, 123-175. b) Cenini, S.; La Monica, G. Inorg. Chim. Acta 1976, 18, 279.
23. Williams, G. D.; Geoffroy, G. L. Organometallics, 1986, 5, 894.
24. (a) Burgess, K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. J. Chem. Soc., Dalton Trans. 1982, 2119-2122. (b) Herrmann, W. A.; Kriechbaum, G. W.; Dammel, R.; Bock, H.; Ziegler, M. L.; Pfisterer, H. J. Organomet. Chem. 1983, 254, 219-241. (c) D'Errico, J. J.; Messerle, L.; Curtis, M. D. Inorg. Chem. 1983, 22, 849-851.

FIGURES

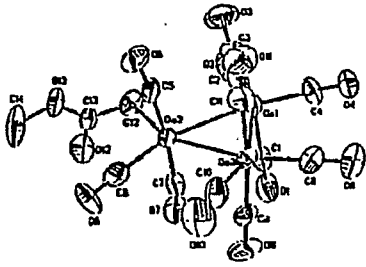


Figure 1

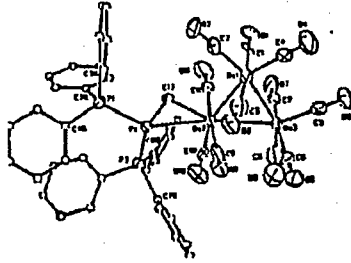


Figure 2

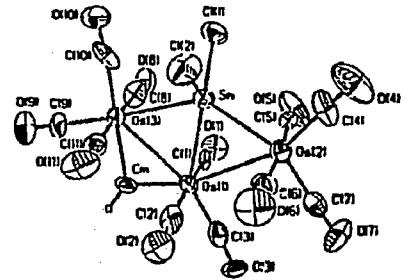


Figure 3

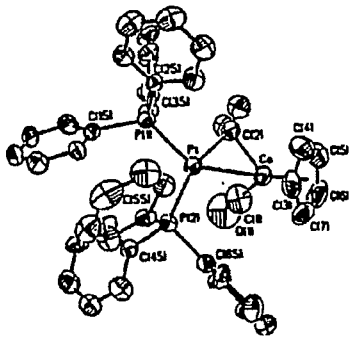


Figure 4

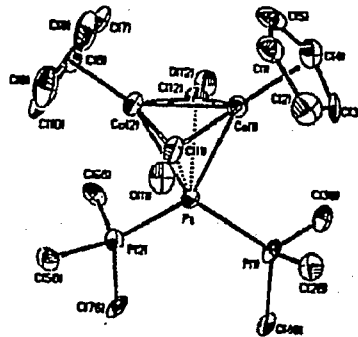


Figure 5

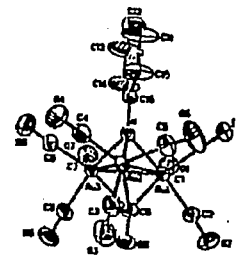


Figure 6

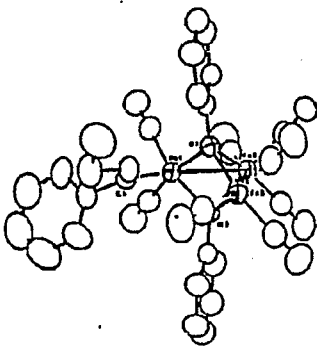


Figure 7

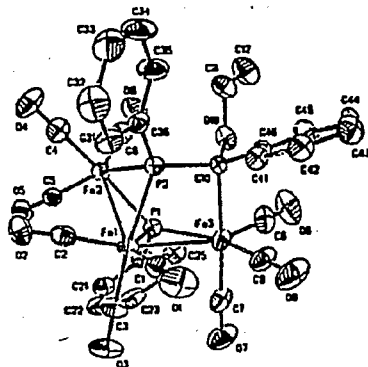


Figure 8

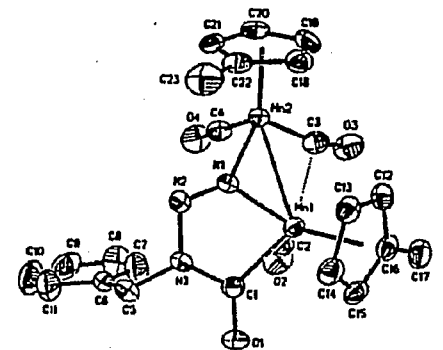


Figure 9