

## TRANSFORMATION OF ORGANIC SUBSTRATES ON METAL CLUSTER COMPLEXES

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**Abstract** - Synthesis and structure determination for the series of complexes  $\text{Fe}_3(\text{N}\equiv\text{CCH}_3)(\text{CO})_9$ ,  $\text{HFe}_3(\text{HN}=\text{CCH}_3)(\text{CO})_9$ ,  $\text{HFe}_3(\text{N}=\text{CHCH}_3)(\text{CO})_9$  and  $\text{H}_2\text{Fe}_3(\text{NCH}_2\text{CH}_3)(\text{CO})_9$  illustrate the stepwise reduction of acetonitrile on the face of a tri-iron complex. Attempts to extend this series to tri-ruthenium and tri-osmium complexes by reaction of the trimetal dodecacarbonyls with aliphatic primary or secondary amines have instead led to the isolation of  $\mu$ -(Q,C) carboxamido complexes  $\text{HM}_3(\text{O}=\text{CNRR}')(\text{CO})_{10}$  (M=Ru or Os; R=H, R'=CH<sub>3</sub> or R=R'=CH<sub>3</sub>). These reactions are accompanied by loss of one mole of carbon monoxide at unprecedented low temperatures for such displacement. Reaction of  $\text{Os}_3(\text{CO})_{12}$  with a variety of nucleophiles (Nu=NR<sub>2</sub><sup>-</sup>, CH<sub>3</sub><sup>-</sup> or OR<sup>-</sup>) in polar media indicate that these attack at carbon of coordinated CO at temperatures below 0°C. The anionic complexes  $[\text{Os}_3(\eta^1\text{-C}(\text{O})\text{Nu})(\text{CO})_{11}]^-$  are formed showing characteristic  $\nu(\text{CO})$  in the infrared in the region 1550 to 1630 cm<sup>-1</sup> (depending on nucleophile and on the extent of ion pairing in the medium). These anions are seen next to lose one mole of carbon monoxide, less readily if ion-paired, to give anions containing a  $\mu$ -(Q,C) bridging group. The latter anions can be protonated to neutral derivatives in overall high yields.

A complex containing a  $\mu$ -(Q,N) bridging group,  $\text{HOs}_3(\text{C}(\text{OH})=\text{NCH}_3)(\text{CO})_{10}$ , is isolated as a minor product in the reaction of  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  with methylisocyanate. The enol isomer exists in equilibrium with a keto form,  $\text{HOs}_3(\text{C}(\text{O})-\text{NHCH}_3)(\text{CO})_{10}$ , enol/keto=95/5 at 25°C in  $\text{CDCl}_3$ . The equilibrium mixture is observed slowly to isomerize to the  $\mu$ -(Q,C) bonded form with a half life of 17.5 d at 25°C ( $E_a$  = 92 kJ/mol in  $\text{CDCl}_3$ ). These studies give new insights<sup>a</sup> into elemental reaction steps that could participate in conversions by metal cluster complexes of CO and H<sub>2</sub> (syngas) into oxygenated derivatives.

## INTRODUCTION

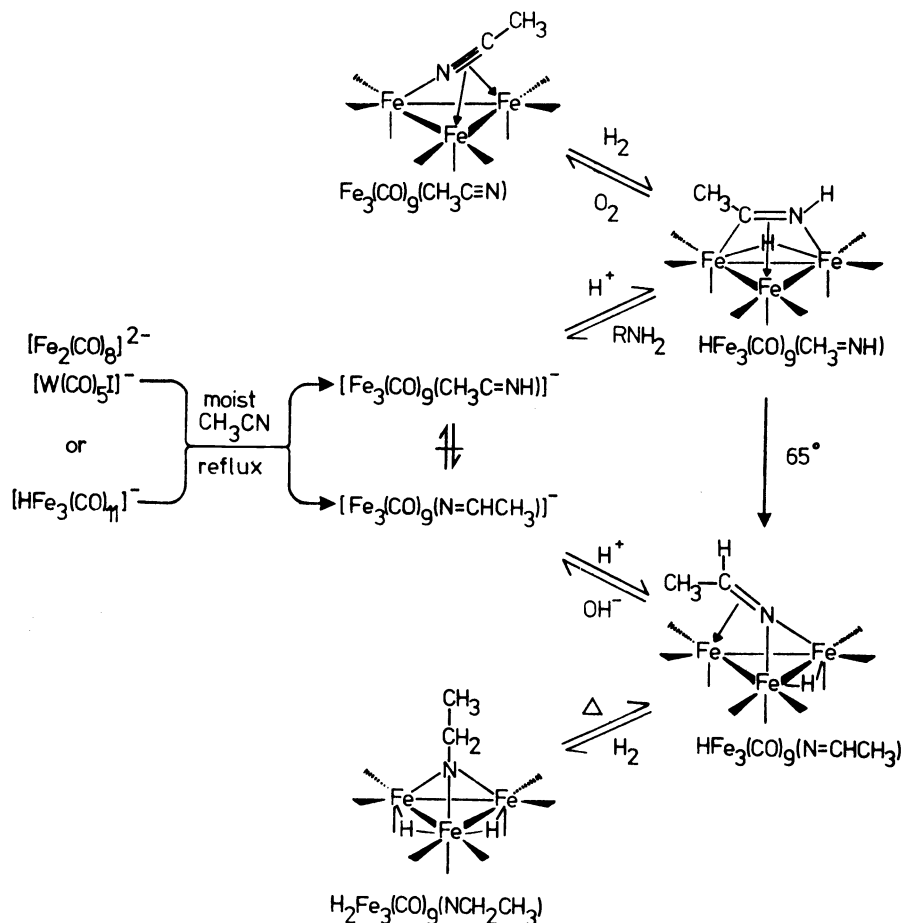
Recent dramatic successes in homogeneous catalysis by transition metal complexes (1) have drawn attention to soluble metal cluster complexes as offering possibilities for transformations of organic substrates as yet unobserved on single metal centers. These expectations stem from observations in heterogeneous systems where certain transformations such as the reduction of dinitrogen to ammonia or the methanation of carbon monoxide are believed to require the cooperative interaction of two or more metal centers (2). A graphic illustration of this is provided by recent isolation of a series of complexes tracing the stepwise reduction of acetonitrile on the face of a tri-iron cluster complex (3). This is described in the first section which follows.

A further tantalizing observation is the production of ethylene glycol from CO and H<sub>2</sub> (syngas) by soluble rhodium catalysts in which the cluster anion  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  is seen as the principal species in the reaction mixture at 180°C (4); production of ethylene glycol under these conditions is promoted by amines and salts at carefully determined concentrations. Such a highly selective conversion of syngas into ethylene glycol has not as yet been achieved under heterogeneous conditions. An understanding of the mechanism

of this transformation is thus of great interest. We believe that the synthesis of complexes containing  $\mu$ -(O,C) coordinated organic groups and the interconversion between  $\mu$ -(N,C) and  $\mu$ -(O,C) coordinated groups which is described in sections which follow after the next provide novel insights into processes which may participate in the reduction and homologation of CO in homogeneous media.

#### STEPWISE REDUCTION OF ACETONITRILE

Our entry into this chemistry came about, as so many other discoveries in organometallic chemistry, by serendipity. Our results are summarized in Scheme 1, below. We were interested initially in preparing mixed metal complexes between iron and Group VI metals such as tungsten or molybdenum. Instead, we obtained tri-iron cluster complexes with coordinated acimidoyl or alkylideneimido groups which were isomeric forms of hydridometalated acetonitrile, the substance we had chosen as solvent for our initial experiments. We have not as yet sorted out the details of this initial synthesis. Some of the experiments we have carried out towards that end are summarized in the full paper which we have published on this subject (3a).

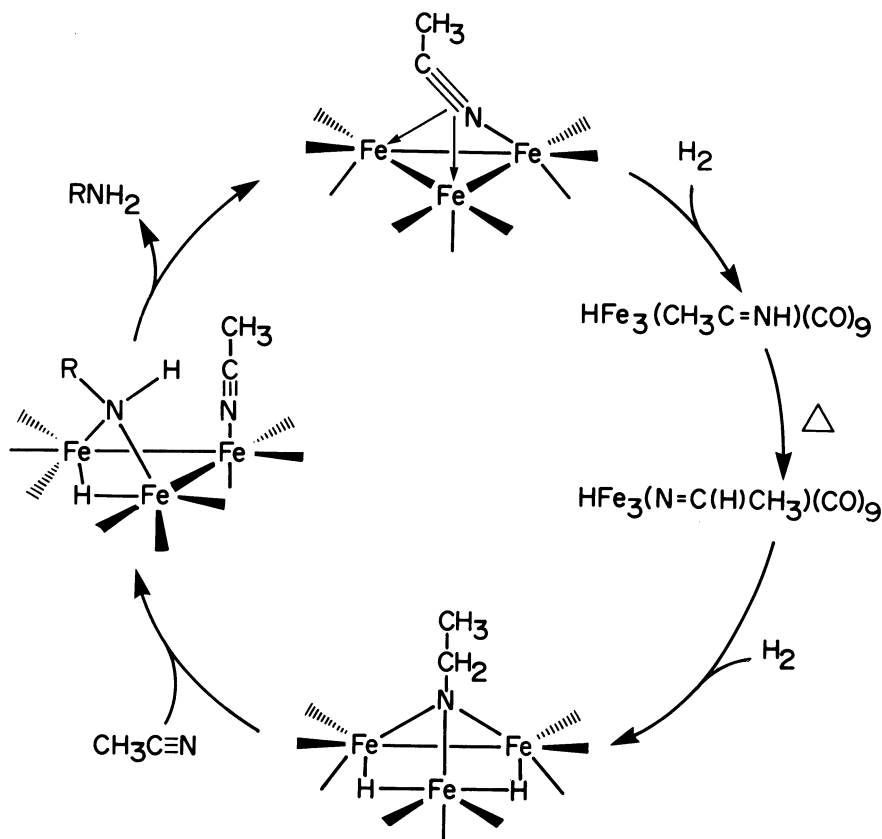


Scheme 1. (Ref. 3) Copyright American Chemical Society (1979); reproduced with permission.

It is clear, however, that the presence of the Group VI metal has a marked effect on the yield even though no mixed metal complexes have as yet been isolated from the reaction mixture; our work-ups have thus far required acidification and chromatographic separation and it may well be that mixed metal carbonyl clusters with an  $\text{Fe}_2\text{Mo}$  core are not stable under these treatments.

It was immediately obvious that the complexes shown in Scheme 1 could be placed into a catalytic cycle. To separate speculation from fact this is

shown in Scheme 2 where the hypothetical intermediate  $\text{HFe}_3(\mu\text{-NHC}_2\text{H}_5)(\text{CO})_9(\text{CH}_3\text{C}\equiv\text{N})$  has been placed into position to complete a catalytic cycle. Such an edge-bridged structure is present in derivatives formed by a variety of bases with tri-metal cluster complexes(5).

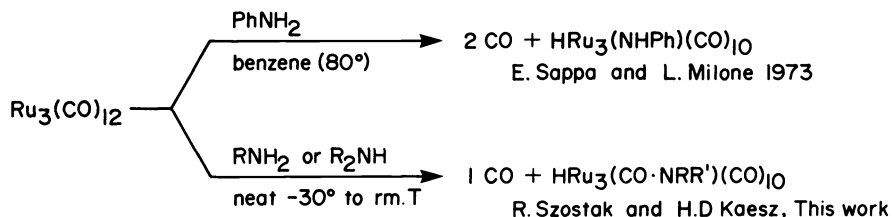


Scheme 2. Proposed catalytic cycle for the reduction of acetonitrile on the face of a tri-iron cluster complex.

Experiments testing the catalytic activity of the isolated cluster complexes shown in Scheme 1 were carried out but to no avail. At temperature and pressure where uptake of hydrogen was first observed ( $180^\circ\text{C}$ , 5,000 psi), the cluster complexes were no longer stable. Examination of the catalytically active mixture revealed colloidal iron suspended in the solution(3d). This is no doubt the active constituent in the patented process for the reduction of nitriles using iron carbonyls as catalyst precursors (6). The remarkably mild conditions (1 atm  $\text{H}_2$ ,  $65^\circ\text{C}$ ) afforded for the reduction of acetonitrile coordinated to the face of the cluster is thus negated by the stability of the dihydrido/ethylnitrene complex. This is however not the only problem for this potential catalytic cycle: due to the high proton acidity of the hydrido-metal carbonyl clusters it is anticipated that amines formed as products would deprotonate any of the intermediate hydrido-metal clusters to give the corresponding anions. This is observed for the isolated complexes as indicated in Scheme 1. The anions, however, do not exhibit the isomerization step  $[\text{Fe}_3(\text{HN}=\text{CCH}_3)(\text{CO})_{10}]^-$  to  $[\text{Fe}_3(\text{N}=\text{CHCH}_3)(\text{CO})_{10}]^-$ , as also indicated in Scheme 1. Thus the molecular process leading to the reduced species would be impeded for anions participating in the cycle. Since substitution of carbonyl groups by phosphine ligands is known greatly to reduce proton acidity in hydrido-metal complexes (7), it may be that a tripod triphosphine ligand sufficiently flexible to permit changes of conformation required at the metal center might lead to a catalytically active cluster complex assuming that the other functions required for such a complex would not be impaired by such a substitution. Studies along these lines are being planned in our laboratory.

FORMATION OF  $\mu$ -(Q,C)-CARBOXAMIDO COMPLEXES

Following discoveries of the tri-iron cluster complexes mentioned above we were interested to investigate whether the same cycle could be obtained for tri-ruthenium complexes. The reaction of  $\text{Ru}_3(\text{CO})_{12}$  with aniline had been reported by Sappa and Milone (5c) to give an edge-bridged complex indicated in the upper line of Scheme 3.



Scheme 3. Comparison of the reactivity of aniline and of primary or secondary aliphatic amines with  $\text{Ru}_3(\text{CO})_{12}$ .

Such a species could provide entry into a reaction cycle as already indicated in Scheme 2 above. We required, however, an aliphatic amine to provide a hydrogen atom on the alpha-carbon atom. We were thus prompted to investigate the reaction of  $\text{Ru}_3(\text{CO})_{12}$  with primary or secondary aliphatic amines with the result shown on the second line of Scheme 3 above (8). Crystal structure determination at low temperature showed the product to be a trimeric cluster complex containing a  $\mu$ -(Q,C)-dimethylcarboxamido group, Fig. 1.

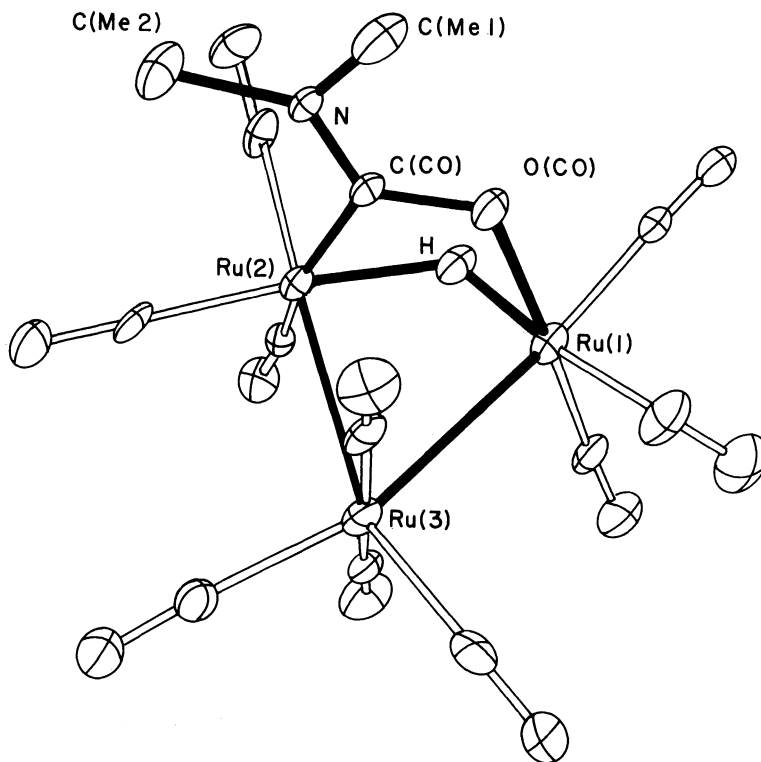
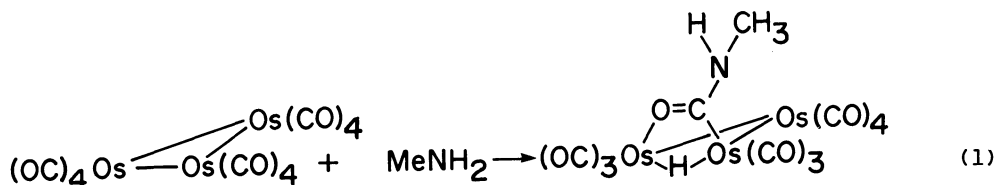


Fig. 1. ORTEP projection for  $\text{HRu}_3(\text{O}=\text{CNMe}_2)(\text{CO})_{10}$  at  $-158^\circ\text{C}$ ; thermal ellipsoids at 50% probability (8).

Selected Distances ( $\text{\AA}$ ):					
Ru(1)-Ru(2)	2.875	Ru(1)-H	1.782	C(CO)-N	1.357
Ru(1)-Ru(3)	2.832	Ru(2)-H	1.887	C(Me1)-N	1.451
Ru(2)-Ru(3)	2.857	Ru(1)-O(CO)	2.100	C(Me2)-N	1.470
		Ru(2)-C(CO)	2.101	C(CO)-O(CO)	1.274

Our initial experiment was carried out with dimethylamine on a minimal quantity of  $\text{Ru}_3(\text{CO})_{12}$ . Excess amine was distilled onto the carbonyl through a short vacuum line. The amine in the reservoir was dried over sodium metal. After transfer of the amine into the reaction tube at  $-196^\circ\text{C}$ , the system was permitted slowly to warm up to room temperature. To our surprise, gas evolution was observed shortly after thawing of the liquid (i.e.  $-30^\circ\text{C}$ ). With excess amine as solvent (i.e. in a polar medium) we were observing displacement of one mole of CO from the triruthenium cluster complex at an unprecedented low temperature. We postulate nucleophilic attack at carbon of coordinated CO by aliphatic amine to give initially an  $\eta^1$ -carboxamido group which must exert a labilizing influence on a CO group either vicinally or geminally coordinated to the cluster. Such ideas derive from the observations of Morris and Basolo of base catalysis in substitution reactions of metal carbonyls (9) and in the observations of Brown and Bellus of a *cis* labilizing effect by the acyl group in acylmanganese carbonyl complexes (10). Angelici has observed a facile substitution in mononuclear carboxamido complexes to occur in position *cis* to this group (11) which is similar to the *cis* labilization of the acyl group discussed by Brown and Bellus. We quickly established that the reaction of a primary amine with  $\text{Os}_3(\text{CO})_{12}$  also leads to a  $\mu$ -(*Q,C*)-carboxamido derivative (12), reaction (1).

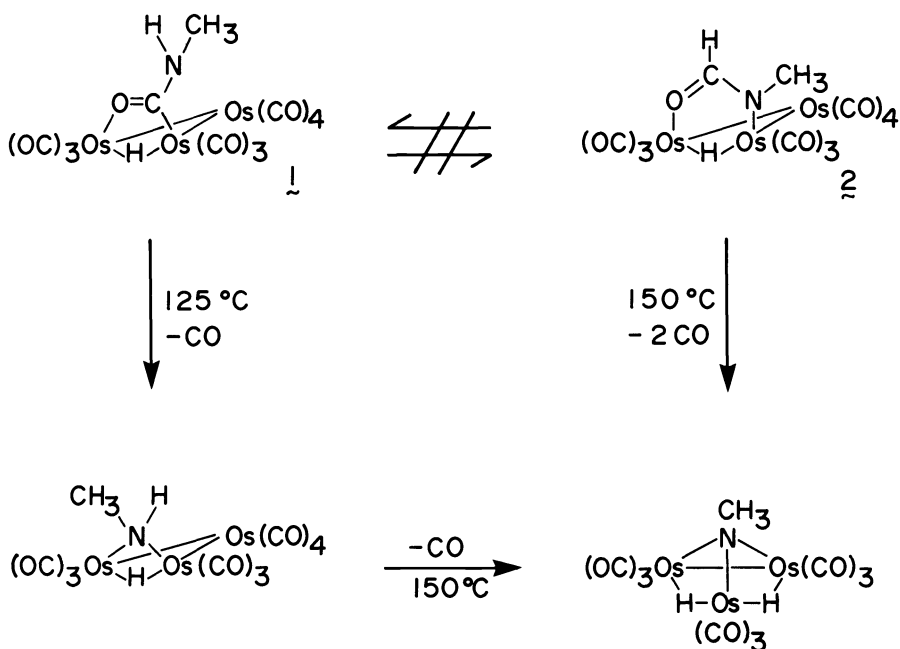


The above transformation is observed to take place at  $-10^\circ\text{C}$  with stirring overnight; the yield of product is 80%. Analogous carboxamido complexes have been reported by Azam, Yin and Deeming (13) in the reaction of  $\text{PhCH}_2\text{NH}_2$  with  $\text{Os}_3(\text{CO})_{12}$  in refluxing octane. These are obtained in lower yield accompanied by the edge-bridged amido complex  $\text{HOS}_3(\text{NHCH}_2\text{Ph})(\text{CO})_{10}$  among other products.

Experiments to elucidate details of the low temperature path to the carboxamido and related  $\mu$ -(*Q,C*)-complexes in polar media are in progress (14). A variety of nucleophiles ( $\text{Nu} = \text{NR}_2^-$ ,  $\text{CH}_3^-$ , and  $\text{OR}^-$ ) are observed to react with  $\text{Os}_3(\text{CO})_{12}$  in tetrahydrofuran solution below  $0^\circ\text{C}$  giving anionic complexes which we formulate as  $[\text{Os}_3(\eta^1\text{-C}(\text{O})\text{Nu})(\text{CO})_{11}]^-$  on the basis of a characteristic absorption in the infrared in the region  $1550$  to  $1630 \text{ cm}^{-1}$  (the position depending on the nucleophile and on the extent of ion-pairing in the medium). These anions are seen next to be transformed, less readily if ion paired, each to another intermediate anion which is converted by acidification to the corresponding neutral  $\mu$ -(*Q,C*)-bridged derivative in high yield. The carboxylato derivatives  $\text{HOS}_3(\text{O}=\text{COR})(\text{CO})_{10}$ ,  $\text{R}=\text{CH}_3$ , or  $\text{C}_2\text{H}_5$ , have been reported earlier to be formed by a similar ionic pathway (15). The low temperature ionic route is the preferred path to formation of  $\mu$ -(*Q,C*)-bridged complexes some of which have previously been obtained by thermal reaction of  $\text{Os}_3(\text{CO})_{12}$  with corresponding amines (13) or aldehydes (16) in hydrocarbon solution.

#### THERMAL CONVERSIONS OF $\mu$ -CARBOXAMIDO COMPLEXES

Shortly after the synthesis of the  $\mu$ -(*Q,C*)-bridged carboxamido complex shown in reaction (1) above, we read with interest of the synthesis of an isomeric  $\mu$ -(*Q,N*)-bridged complex  $\text{HOS}_3(\text{O}=\text{C}(\text{H})\text{N-pCH}_2\text{Ph})(\text{CO})_{10}$  obtained in 80% yield by Adams and Golembeski in the reaction of  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  with *p*-tolylisocyanate (17). We were curious to know whether the  $\mu$ -(*Q,C*)-bridged form could be thermally converted to the  $\mu$ -(*Q,N*)-bridged form, or *vice-versa*. Our experiments are summarized in Scheme 4 (next page). For these experiments we synthesized the analogous  $\mu$ -(*Q,N*)-bridged complex  $\text{HOS}_3(\text{O}=\text{C}(\text{H})\text{NCH}_3)(\text{CO})_{10}$  from methylisocyanate and  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  (18) following the work of Adams and Golembeski (17). A more detailed description of the reaction mixture is presented in Scheme 5 below together with a discussion of the minor by-products which Y.C.Lin isolated in this reaction. Returning to Scheme 4, the  $\mu$ -(*Q,C*) and  $\mu$ -(*Q,N*)-bridged complexes proved not to be thermally interconvertible; this observation was recently also reported by the Adams group (19). We find that heating of each of these complexes leads to decarbonylation products as indicated in Scheme 4.

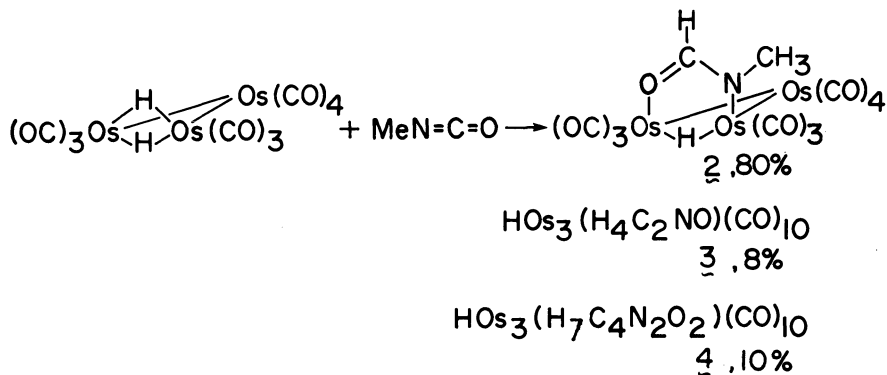


Scheme 4. Thermal conversions of carboxamido complexes.

The reaction shown on the left of the Scheme was also reported by Azam, Yin and Deeming (13). The three atom  $\mu$ -(Q,N)-bridged isomer seems to be thermally more stable and its decomposition does not occur until 150°C. The increased thermal stability will play a role in our interpretation of these reactions in terms of possible homologation of CO to C<sub>2</sub>-oxygenates taken up in the last section. It is also worth noting in passing that an ethyl analogue of the triply-bridged nitrene complex shown at the lower right of Scheme 4 would provide us with an entry for a tri-osmium cycle similar to that shown for the tri-iron complexes in Scheme 1 above.

ISOLATION OF A  $\mu$ -(N,C)-BRIDGED FORMAMIDO COMPLEX AND ITS ISOMERIZATION TO A  $\mu$ -(Q,C)-BRIDGED COMPLEX

A most interesting result derives from two minor products obtained in the low temperature reaction of methylisocyanate with H<sub>2</sub>Os<sub>3</sub>(CO)<sub>10</sub>, see Scheme 5.



Scheme 5. Principal products obtained in the reaction of H<sub>2</sub>Os<sub>3</sub>(CO)<sub>10</sub> with methylisocyanate (18).

Complex **3** proved to be unstable converting to the known  $\mu$ -(O,C)-bridged complex with a half-life of 17.5 days at 25°C in CHCl<sub>3</sub> solution. This is shown in Scheme 6 below. Measurement of the rate of isomerization over the temperature range 25 to 60°C permits us to calculate the activation energy for this process to be 92 kJmol<sup>-1</sup> in CDCl<sub>3</sub>. We were not able to obtain single crystals of **3**; assignment of its structure is based on spectroscopic data which is presented after a discussion of **4**. Single crystals of **4** were obtained and a structure determined at low temperature, see Fig. 2.

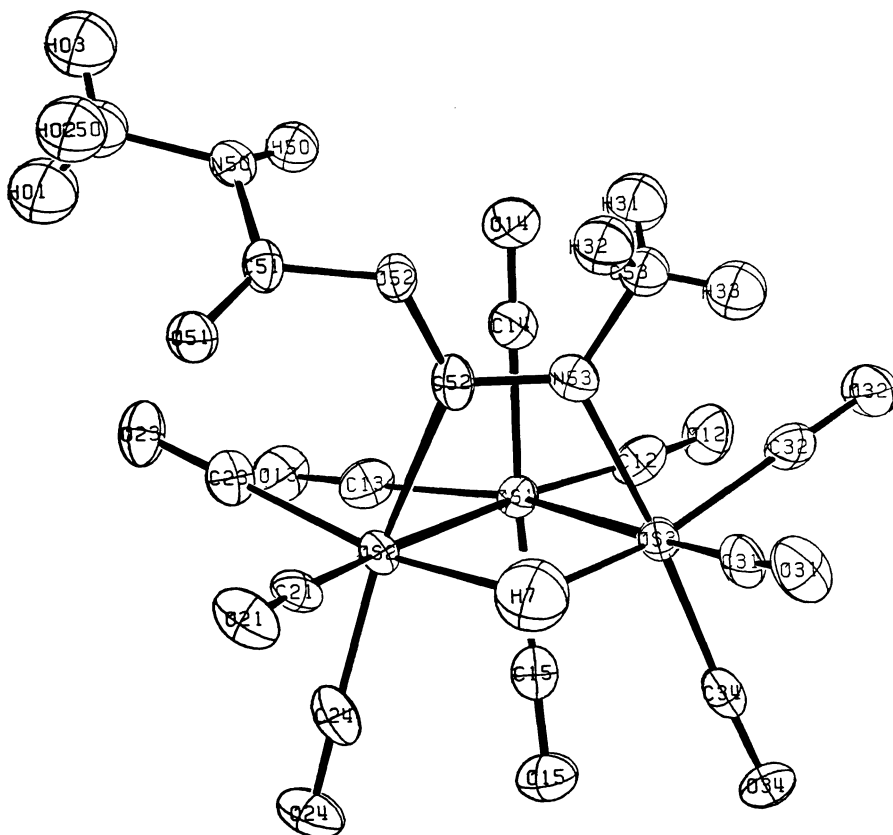


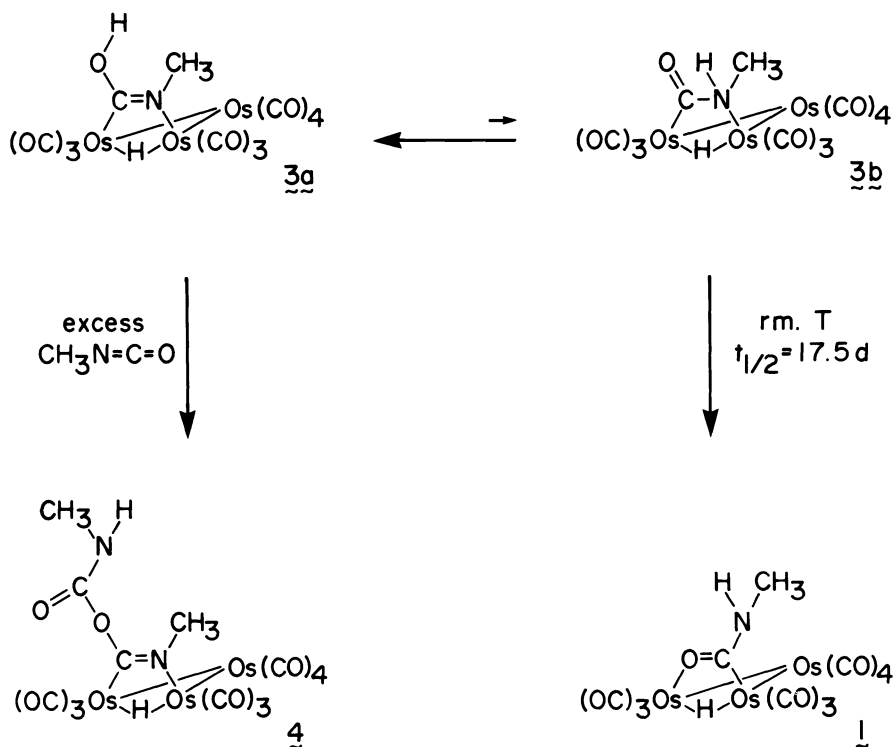
Fig. 2. ORTEP projection for HO<sub>3</sub>(C(OR)=NCH<sub>3</sub>)(CO)<sub>10</sub>, R = C(O)N(H)CH<sub>3</sub>, at -158°C (18); thermal ellipsoids at 50% probability. Copyright American Chemical Society (1981); reproduced with permission. Selected distances and angles:

Os(1)-Os(2)	2.882 Å	C(52)-N(53)	1.27 Å	C(21)Os(2)H(7)	84°
Os(1)-Os(3)	2.882	N(53)-C(53)	1.47	C(31)Os(3)H(7)	80
Os(2)-Os(3)	2.924	C(52)-O(52)	1.36	C(23)Os(2)Os(1)	89
Os(2)-H(7)	1.96	C(51)-O(52)	1.40	C(32)Os(3)Os(1)	85
Os(3)-H(7)	1.72	C(51)-O(51)	1.21	C(23)Os(2)H(7)	172
Os(2)-C(52)	2.13	C(51)-N(50)	1.33	C(32)Os(3)H(7)	171
Os(3)-N(53)	2.12				

Standard Distances (Å) (20)

C-N	1.49	C-O	1.43
C=N	1.29	C=O	1.20
C≡N	1.15	d <sub>(CO)</sub>	1.128

From its structure, **4** is recognized as a urethane complex derived from the reaction of excess methylisocyanate with a suitable hydroxylic precursor of **4**. This might very well be the enol tautomer of a  $\mu$ -(N,C)-bonded imidoyl derivative tentatively assigned as one of two possible isomeric structures for **3**. Fortunately at the temperature of our reaction (25°C) there was only partial conversion of **3** into **4**; this is shown on the left hand side of Scheme 6 (see next page). The isomerization of **3** into **1** is shown at the right hand side of this Scheme. We are now in position to examine and interpret the spectroscopic data which are in support of the tautomeric structure-pair for



Scheme 6. Proposed tautomeric structures for 3 and their relationship to the isolated products 4 and 1 (18).

derivative 3. First we examine the infrared spectra for complex 4. These are shown on the next page, in Fig. 3. The absorptions derived from the known functional groups in this derivative are assigned on the lower trace according to their characteristic frequencies (21). In particular we see an absorption at  $1590 \text{ cm}^{-1}$  which is somewhat below  $1650 \text{ cm}^{-1}$  expected for  $\nu(\text{C}=\text{N})$  (21). This correlates well with the bond distance C(52)-N(53) of  $1.27 \text{ \AA}$  which is just under  $1.29 \text{ \AA}$  for a "standard" carbon to nitrogen double bond (20). For optimal display of the metal carbonyl region an expanded spectrum in hexane solution is given in the top trace. Two of the characteristic absorptions previously identified in the lower trace can also be seen in the upper trace. These consist of the band assigned as  $\nu(\text{C}=\text{O})$  (of the urethane group) and the band assigned as  $\nu(\text{C}=\text{N})$  (of the imidoyl group). Neither of these have changed in relative intensity, an important point to contrast with analysis of the spectra of 3 which follows.

The infrared spectra of 3 are shown in Fig. 4 on the page after the next. In the lower trace obtained in  $\text{C}_2\text{Cl}_4$ , one can see the classic absorptions for an hydroxyl group: a sharp band at  $3595 \text{ cm}^{-1}$  (free -OH) accompanied by a broad band at lower energy centered at  $3313 \text{ cm}^{-1}$  (hydrogen-bonded -OH) (21). The methyl group is similarly clearly indicated by the three absorptions around  $2900 \text{ cm}^{-1}$  (three due to classic Fermi resonance of one of the two fundamental stretching modes of the  $\text{CH}_3$  group with the first overtone,  $2 \times 1457 \text{ cm}^{-1}$ , of the methyl deformation mode). An absorption for  $\nu(\text{C}-\text{O})$  is seen at  $1255 \text{ cm}^{-1}$  and that for  $\nu(\text{C}=\text{N})$  is seen at  $1616 \text{ cm}^{-1}$ . Hexane solution was then investigated for optimum resolution of the metal carbonyl bands (upper trace); here we observed a band at  $1792 \text{ cm}^{-1}$  in the region for  $\nu(\text{C}=\text{O})$  comparable in intensity to that of the  $\nu(\text{C}=\text{N})$  band now at  $1618 \text{ cm}^{-1}$ . The  $\nu(\text{C}=\text{O})$  band was present at only trace intensity in the  $\text{C}_2\text{Cl}_4$  solution. The varying intensity of the  $\nu(\text{C}=\text{O})$  band in solvents of varying polarity suggested to us shifts in a keto/enol equilibrium. We thus returned for a closer look at the  $^1\text{H}$  NMR spectrum for further evidence of this phenomenon. An  $^1\text{H}$  NMR spectrum for 3 taken 24 days after initial solution is shown in Fig. 5; this is displayed immediately following the figures of the infrared spectra on the next two pages.



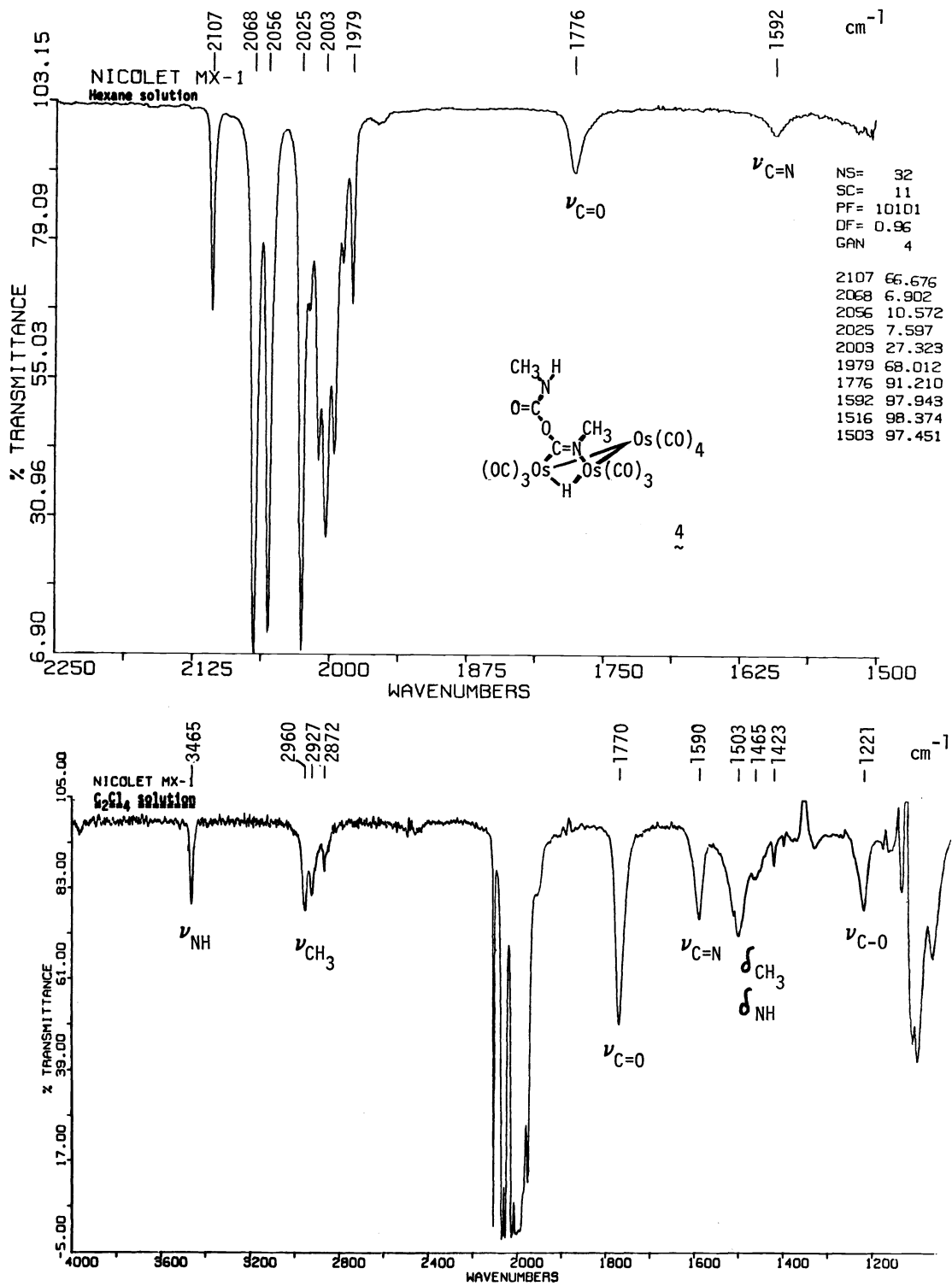


Fig. 3. Infrared spectra for **4**,  $\text{HOs}_2(\text{C}(\text{OR})=\text{NCH}_3)(\text{CO})_{10}$ ,  $\text{R} = \text{C}(\text{O})\text{N}(\text{H})\text{CH}_3$ ; Nicolet MX-1 FT Spectrometer. Upper trace hexane solution; lower trace  $\text{C}_2\text{Cl}_4$  solution.

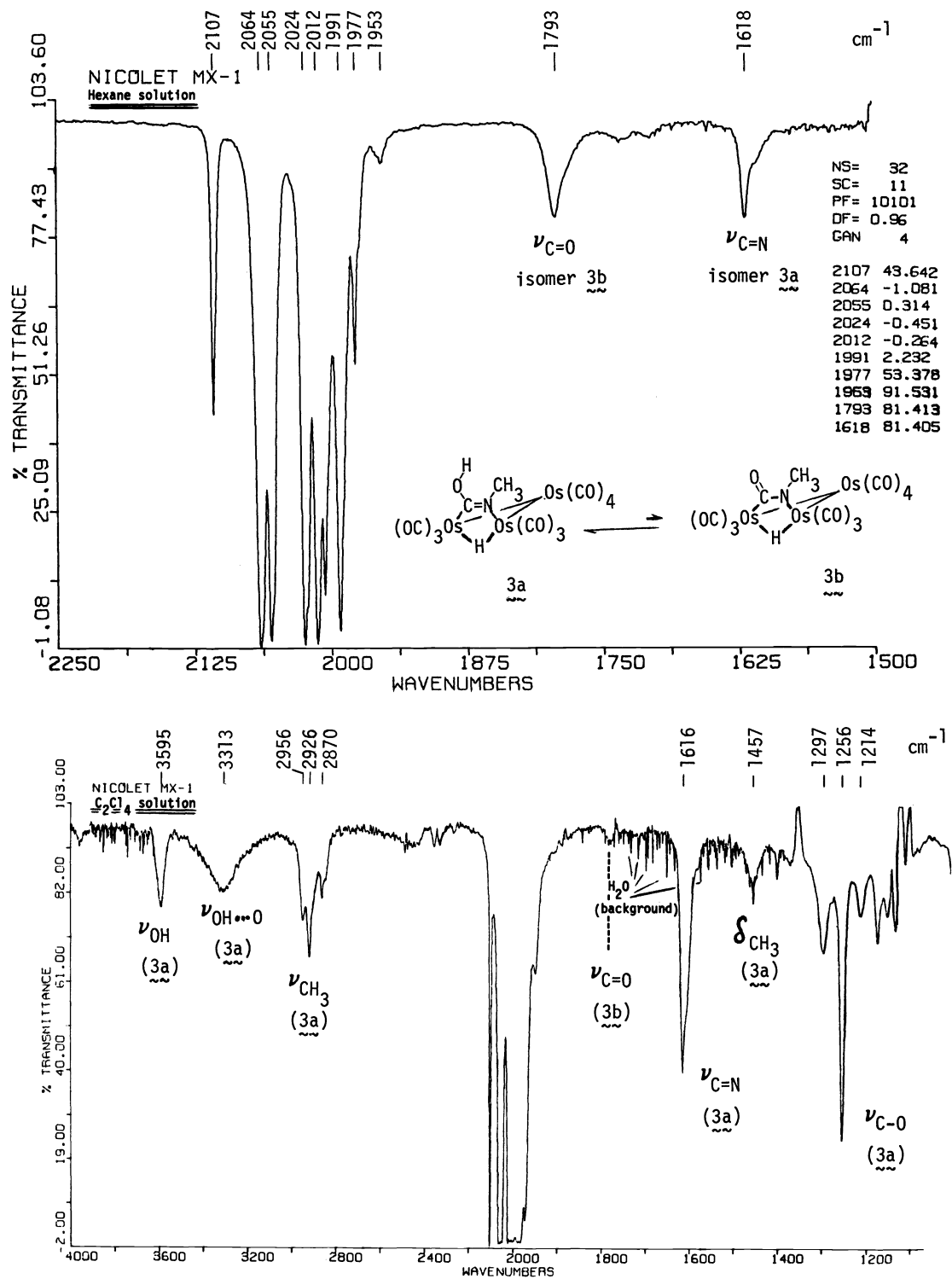


Fig. 4. Infrared spectra for 3; Nicolet MX-1 FT Spectrometer. Upper trace, hexane solution; lower trace, C<sub>2</sub>Cl<sub>4</sub>.

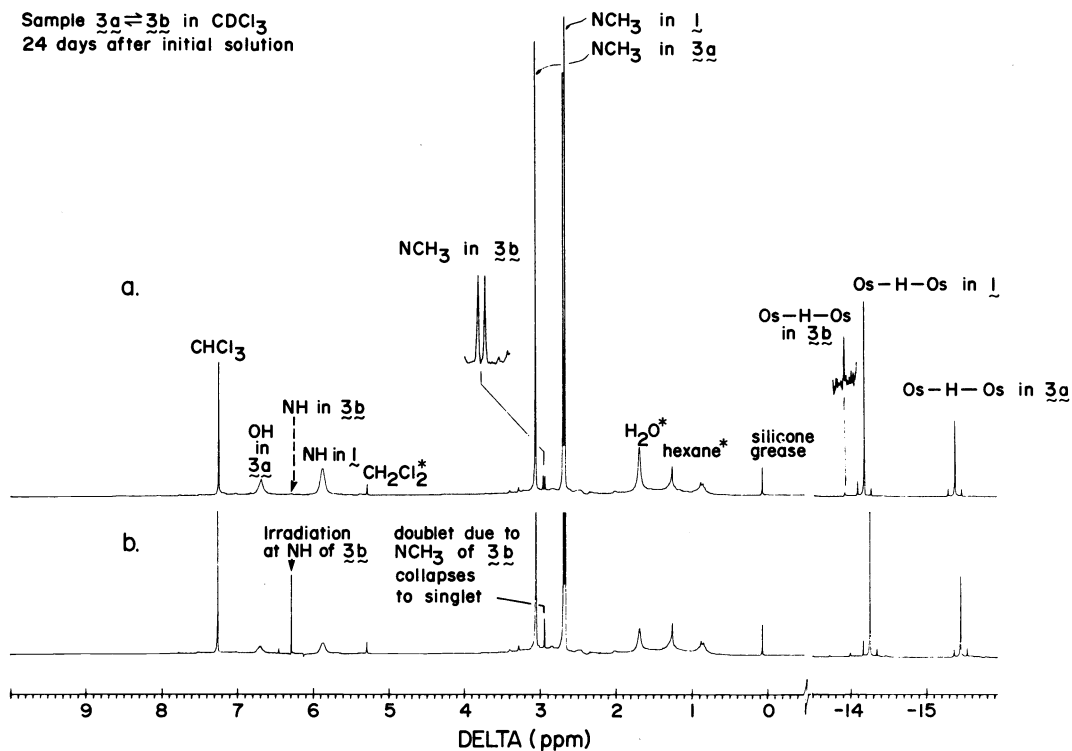


Fig. 5.  $^1\text{H}$  NMR spectra of  $\underline{3}$ , 24 days after initial solution, Bruker WP 200. Upper trace, un-decoupled spectrum; lower trace, double irradiation at the position indicated.

By  $^1\text{H}$  NMR spectra such as shown in Fig.5 we first learned of the transformation of  $\underline{3}$  into  $\underline{1}$  (Scheme 6). Spectra of  $\underline{3}$  at various intervals of time after the purified  $\underline{3}$  derivative was put into solution showed varying quantities of  $\underline{1}$ .

The resonances of  $\underline{1}$  could be confirmed by the independent isolation of this derivative from the reaction of methylamine and  $\text{Os}_3(\text{CO})_{12}$ , reaction (1) above. We see a doublet for the methyl group on nitrogen in  $\underline{1}$  accompanied by the broadened resonance of the NH proton and the sharp high field resonance of hydrogen bridging an edge of the metal triangle. This latter is surrounded by the characteristic  $^{187}\text{Os}$  satellites.

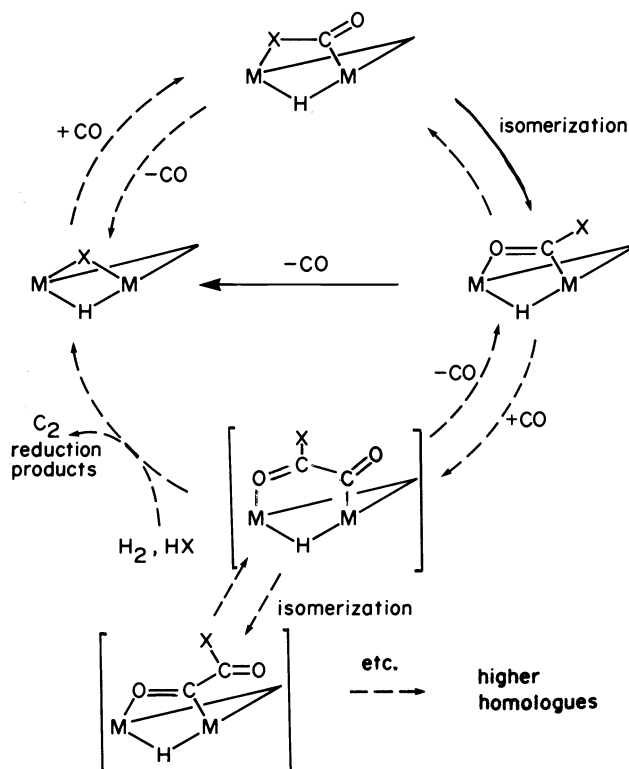
Having passed more than one half-life in the conversion of  $\underline{3}$  into  $\underline{1}$  in the spectrum shown in Fig. 5 there is less of  $\underline{3}$  in solution than there is of  $\underline{1}$ ; this is best seen in the high field resonances at the right of the spectra. Other resonances of  $\underline{3}$  are the singlet for the methyl group on nitrogen in the  $\underline{enol}$  tautomer,  $\underline{3a}$ , the principal isomer of  $\underline{3}$  in solution, and the broadened resonance of the  $-\text{OH}$  group.

For evidence of the  $\underline{keto}$  form,  $\underline{3b}$ , closer inspection of the upper trace in Fig. 5 is required. This reveals a small doublet due to the resonance of the methyl group which is coupled to the geminally bonded hydrogen atom in this tautomer. This doublet is displayed at enhanced intensity just above the upper trace. To prove that this is a resonance coupled to a hydrogen atom on nitrogen we resorted to double resonance. It was evident to us that due to the relatively low concentration of isomer  $\underline{3b}$  we could not really expect to see the broadened resonance of its NH proton; Y.C.Lin however spotted a suspicious bump in the NH region not visible in the reduced spectrum displayed in Fig. 5, but indicated by the dashed line. This is where he started the double resonance experiment and this led exactly to collapse of the aforementioned doublet into a singlet as shown on the lower trace. Finally the high field region was scanned and another suspicious bump was intensified to show appropriate enhancement in the surrounding base line where the  $^{187}\text{Os}$  satellites would be expected confirming this as the resonance for the hydrogen bridging an edge of the osmium triangle in the  $\underline{keto}$  tautomer. The proton NMR

permits us to estimate the relative concentrations of the two tautomers as 95/5, enol/keto. This tautomerism is rapid on the laboratory time frame but slow on the NMR time frame.

#### SUMMARY AND CONCLUSIONS

We were quite prepared at this point in our work to be satisfied with contemplation of the intrinsic beauties of the processes which nature had permitted us to discover. However, as attributed to Charles Darwin that... "there can be no good and original observation without speculation,".. we were challenged to see what connection there might be between this chemistry and practical questions in catalysis facing us today. We introduce Scheme 7 at this point to be discussed after the following paragraph in which we first offer some comments relating to the reduction of acetonitrile.



Scheme 7. Relationships of observed and [proposed] cluster species for syngas conversion. Copyright American Chemical Society; reproduced with permission.

The reduction of acetonitrile in the first part of this paper shows how easy it is to reduce this substrate with elemental hydrogen once the acetonitrile is coordinated to the face of the metal cluster. The pattern of reduction is intriguing; this results in the delivery in each of the reduction steps of one atom of hydrogen on the substrate and one on the metal cluster. This of course does not say anything about the mechanism of this process; this very likely involves oxidative addition of elemental hydrogen at a point of coordinative unsaturation at a single metal center followed by migration of one of the added hydrogen atoms to the coordinated substrate. These processes translate without much difficulty to reactions which could occur at homo- or hetero-polymetallic centers on surfaces of solids. Our evidence does not justify further printed speculation on this subject but it is just those types of insights that are a rich source for new experimentation. Readers are thus invited to engage in their own speculations about the significance of our results which we earnestly wish will lead them to fruitful discoveries.

Regarding the observations on the  $\mu$ -carboxamido complexes and their interconversions, perhaps we can venture some speculation which does not too far outrun our data. This has been summarized in Scheme 7 above. The transformations observed in this work are represented by solid arrows in the

Scheme with X = NHMe. These supplement proposals recently advanced by Wilkinson and co-workers (22). In the top portion of the Scheme a possible role of a  $\mu$ -(X,C)-bridged species is indicated in decarbonylation of the  $\mu$ -(Q,C)-bridged species, or its reverse. Decarbonylations have been observed by us and others discussed above (Scheme 4). In the lower portion of Scheme 7 the construction of a 1,2-dioxygenate is proposed by carbonyl insertion into the  $\mu$ -(Q,C)-bridged species. Such a double migration is unfavored at single metal centers with the rare exception of the interesting report by Des Abbayes and Buloup (23). At the bi-metallic centers illustrated in Scheme 7, such a double migration might be favored by the additional driving force provided by expansion of what can be formally viewed as a five-membered ring in the  $\mu$ -(Q,C)-bridged species to a six membered ring in the carbonyl inserted products. Experiments to confirm or deny these postulates are in progress.

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