

MELDOLA MEDAL LECTURE*

The Relationship between Metal Carbonyl Clusters and Supported Metal Catalysts

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1 Introduction

An important class of heterogeneous catalysts consists of small metal particles (with average diameters of ~ 1 to ~ 20 nm) dispersed on a high surface area oxide support.¹ These materials are heterogeneous in many senses since both the metal particle sizes and oxide supports are non-uniform and this makes it virtually impossible to describe their chemistry on a molecular level. For example, a wide variety of potential chemisorption sites exist and it is difficult, on the basis of any spectroscopic or chemical probe, to ascertain which ones are occupied by a substrate. In the past few years, studies of the chemistry of single-crystal metal surfaces have markedly increased the understanding of chemisorption processes.² However, even in these idealized cases, identifying adsorption modes can be difficult.

Transition-metal carbonyl clusters are an ever extending class of complexes, which can be isolated and their structures determined by the conventional methods of *X*-ray diffraction, vibrational spectroscopy, and nuclear magnetic resonance.³ Presently, complexes with up to 38 metal atoms are known.⁴ There is an appealing parallel between cluster complexes and metal surface chemistry, which has been reviewed at length.⁵ In this review we shall discuss two contributions that cluster chemistry can make to surface studies, *viz.*, as structural models and catalyst sources.

2 Clusters as Structural Models

A. Metal Polyhedra.—A summary of the metal skeletons adopted for tri- to

*Based on the lecture given on 25th September, 1980, at the Autumn Meeting, University College, Cardiff.

¹ J. R. Anderson, 'Structure of Metallic Catalysts', Academic, New York, 1975.

² *e.g.*, J. C. Buchholz and G. A. Somorjai, *Acc. Chem. Res.*, 1976, **9**, 333; G. A. Somorjai, *ibid.*, p. 248.

³ B. F. G. Johnson, ed., 'Transition Metal Clusters', Wiley, New York, 1980.

⁴ P. Chini, *J. Organomet. Chem.*, 1980, **200**, 37.

⁵ E. L. Muetterties, T. N. Rodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, 1979, **79**, 91; E. L. Muetterties, *Isr. J. Chem.*, 1980, **20**, 84.

hexa-nuclear metal carbonyl clusters is given in Table 1. In each case, the most commonly found geometry is listed first and is in accord with chemical intuition.

Table 1 Geometries of tri- to hexa-nuclear metal skeletons in metal carbonyl clusters

No of metals	Metal polyhedron	Example
3	Triangular	$M_3(CO)_{12}$ (M = Fe, Ru, Os) ^a
	Linear	$Os_3(CO)_{12}I_2^a$
	Bent	$HRe_3(CO)_{14}^a$
4	Tetrahedron	$M_4(CO)_{12}$ (M = Co, Rh, Ir) ^a
	Butterfly	$[HFe_4(CO)_{13}]^-^a$
	Planar, D_{2h}	$[Re_4(CO)_{16}]^{2-}^a$
	Triangular + 1 terminal	$[H_4Re_4(CO)_{15}]^{2-}^a$
5	Trigonal bipyramid	$[Os_5(CO)_{15}]^{2-}^a$
	Square pyramid	$M_5C(CO)_{15}$ (M = Fe, Ru, Os) ^a
	Edge bridged tetrahedron	$H_2Os_5(CO)_{16}^a$
	Vertex linked triangles (planar)	$[Fe_4Pd(CO)_{12}]^{2-}^b$
	(skewed)	$Os_5(CO)_{19}^c$
6	Triangle + 2 terminal	$H_2Os_3Re_2(CO)_{20}^d$
	Octahedron	$M_6(CO)_{16}$ (M = Co, Rh, Ir) ^a
	Trigonal prism	$[Pt_6(CO)_{12}]^{2-}^a$
	Capped trigonal pyramid	$Os_6(CO)_{18}^a$
	Capped square pyramid	$H_2Os_6(CO)_{18}^a$

^a P. R. Raithby in ref. 3, p. 5; ^b G. Longoni, M. Manassero, and M. Sansoni, *J. Am. Chem. Soc.*, 1980, **102**, 3242; ^c D. H. Farrar, B. F. G. Johnson, J. Lewis, J. N. Nicholls, P. R. Raithby, and M. J. Rosales, *J. Chem. Soc., Chem. Commun.*, 1981, 273; ^d J. R. Shapley, G. A. Pearson, M. Tachikawa, G. E. Smidt, M. R. Churchill, and F. J. Hollander, *J. Am. Chem. Soc.*, 1977, **99**, 8064.

However the geometry of a metal skeleton in a particular complex is dependent upon both electronic and steric effects. Two electron counting procedures are commonly applied to these systems, *viz*, the effective atomic number rule, assuming each edge of the skeleton to be equivalent to a two-electron bond, and the skeletal electron counting rules.⁶ Neither of these systems is reliable, although the latter scheme is fairly effective when the majority of the skeletal vertices are isolobal with the BH units for which these rules were formulated, *e.g.*, $M(CO)_3$.⁷ For example, the reduction of $Os_6(CO)_{18}$ to its dianion is accompanied by a skeletal change from a capped trigonal bipyramid to an octahedron.⁸ These structures would be anticipated for six and seven skeletal pairs, respectively. On the other hand, protonation of $[Fe_4(CO)_{13}]^{2-}$ to give $[HFe_4(CO)_{13}]^-$, which involves no change in the total number of electrons, also causes a change in metal

⁶ K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

⁷ M. Elian and R. Hoffman, *Inorg. Chem.*, 1976, **15**, 1148.

⁸ C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1976, 302; M. McPartlin, C. R. Eady, B. F. G. Johnson, and J. Lewis, *ibid.*, p. 883.

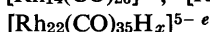
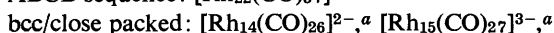
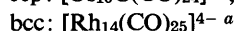
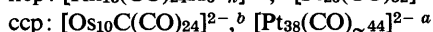
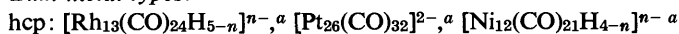
geometry, from a tetrahedron to a butterfly.⁹ This is probably due to the steric problem of accommodating 14 ligands around an iron tetrahedron, and is possible for the larger osmium system.¹⁰

This is not a simple situation to apply to supported small metal particles. For each nuclearity there is a choice of geometries that is influenced by the ligands and so the structures of supported metal particles may well alter under catalytic reaction conditions. Metal particles of this size range are very difficult to study and estimations of particle size are made on the basis of chemisorption and electron microscopy measurements. Even then, reports of particle shape are rare. Electron micrographs of a sample of 1% rhodium on silica gel were thought to show individual metal atoms (2.7 Å diameter of 2.69 Å in the metal).¹¹ A pentagon of rhodium atoms 3.75 Å apart (too distant for metal-metal bonding) was thought to be discernible. There has been a more recent attempt to observe the structure of supported rhodium,¹² but in this case the particles were much larger (~ 20 Å).

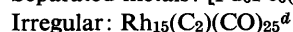
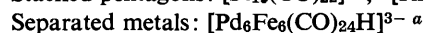
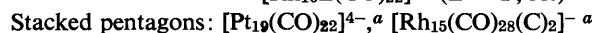
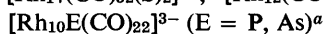
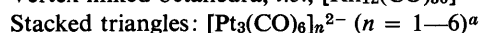
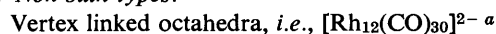
The structural classes of the larger metal carbonyl clusters are shown in Table 2. $[\text{Pt}_{38}(\text{CO})_{\sim 44}]^{2-}$ represents the largest yet identified and the diameter of the metal skeleton in that complex is 11.6 Å.⁴ This is comparable with the average

Table 2 Structural classes of larger metal carbonyl clusters (> 9 metal atoms)

(a) Bulk metal types:



(b) Non-bulk types:



^a Ref. 4; ^b P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 224; ^c J. L. Vidal, *Inorg. Chem.*, 1981, 20, 243; J. L. Vidal, W. E. Walker, and R. C. Schoening, *ibid.*, p. 238; ^d V. G. Albano, P. Chini, S. Martinengo, M. Sansoni, and D. Strumolo, *J. Chem. Soc., Dalton Trans.*, 1978, 459; ^e J. L. Vidal, R. C. Schoening, and J. M. Troup, *Inorg. Chem.*, 1981, 20, 227

⁹ M. Manassero, M. Sansoni, and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 1976, 919.

¹⁰ P. A. Dawson, B. F. G. Johnson, J. Lewis, D. A. Kaner, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, 961.

¹¹ E. B. Prestridge and D. J. C. Yates, *Nature (London)*, 1971, 234, 345.

¹² B. Tesche, H. Knözinger, and B. C. Gates, *J. Catal.*, 1980, 64, 235.

diameters reported for many highly dispersed supported metal catalysts. Thus on the basis of size, this class of complex overlaps with the smaller supported metal particles, and they may represent a similar situation to the latter when exposed to carbon monoxide. The variety of structural forms is striking. Several of these are fragments of bulk metal structures, but there is also an extensive series of other skeletal forms. These alternative structures are particularly favoured by interstitial heteroatoms, but carbonylate anions also adopt non-bulk forms. The five-fold symmetry¹³ of $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ is reminiscent of some of the favoured forms of small arrays of atoms predicted from Leonard Jones potential calculations.¹⁴ A centred icosahedron rather than a centred cubo-octahedron (the ccp fragment) was predicted for a 13-atom assembly. The preferred 19-atom structure is compared to the skeleton of the platinum complex in Figure 1 and the difference is only in the relative orientations of the three pentagons. Interestingly, the diffraction interference patterns obtained for amorphous metal-containing materials, *e.g.*, NiP and PdSi, are close to those calculated for a centred icosahedron.¹⁵

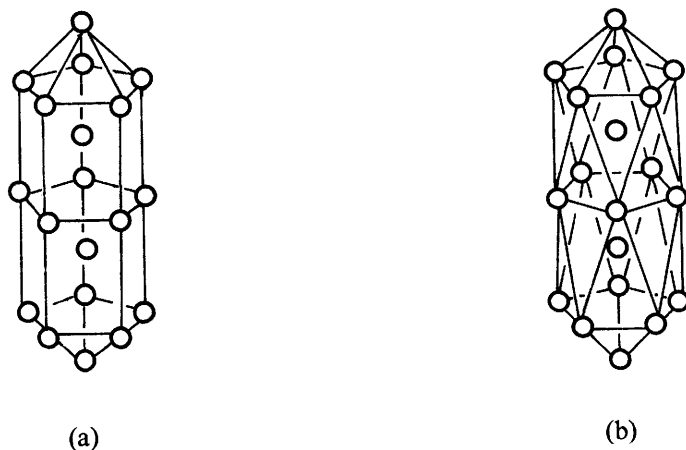


Figure 1 Metal polyhedra of (a) $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ and (b) calculated for a 19-atom array

B. Ligand Sites.—Polynuclear metal complexes offer the types of ligand sites that are also likely to be available to a substrate on a metal surface. Carbonyl complexes have been used for many years as a data bank for assigning vibrational data recorded on chemisorbed CO, and the frequencies of the $\nu(\text{CO})$ bands used to differentiate between terminal ('atop') and bridging (either μ_2 or μ_3) sites. The chemisorption of carbon monoxide to alumina-supported rhodium provides

¹³ D. M. Waschecheck, E. J. Wucherer, L. F. Dahl, A. Ceriotti, G. Longoni, M. Manassero, M. Sansoni, and P. Chini, *J. Am. Chem. Soc.*, 1979, **101**, 6110.

¹⁴ M. R. Hoare and P. Pal, *J. Cryst. Growth*, 1972, **17**, 77; *Adv. Phys.*, 1971, **20**, 161.

¹⁵ C. L. Briant, *Discuss Faraday Soc.*, 1976, **61**, 25.

a good example of this approach. Three types of site have been identified by infrared spectroscopy.¹⁶ Two of these are probably Rh-CO (ν_{CO} 2070 cm^{-1}) and μ_2 -Rh-CO (ν_{CO} 1870 cm^{-1}) units on rhodium particles, and these frequencies correlate well with those observed for CO (surface coverage of $\frac{1}{2}$) on an exposed close-packed rhodium plane (111) by electron energy loss spectroscopy (EELS).¹⁷ Two other bands occur at 2101 and 2031 cm^{-1} , and although there has been a suggestion that these are due to dicarbonyl sites on the edges of two-dimensional rafts,¹⁸ ^{13}C n.m.r. evidence indicates that these are from isolated $\text{Rh}^{\text{I}}(\text{CO})_2$ metal centres.¹⁹

Recently, new carbonyl bonding modes have been identified that should also be considered in surface studies (Figure 2). The dinuclear complex (1) contains both a semibridging (ν_{CO} 1700 cm^{-1}) and a π -bonded carbonyl group (ν_{CO} 1560

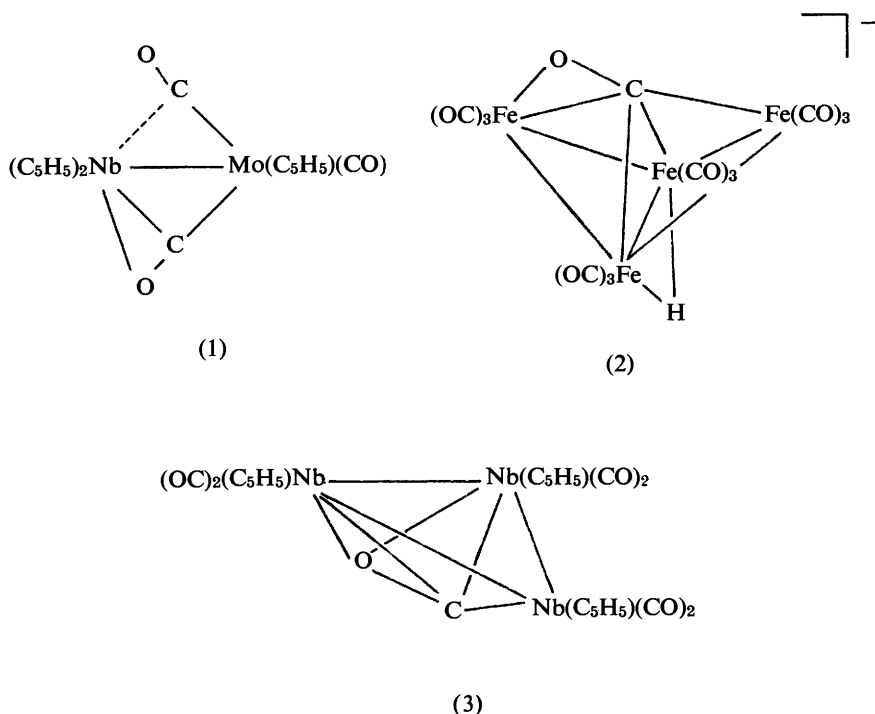


Figure 2 Examples of π -bonded carbonyl ligands

¹⁶ J. T. Yates, jun., T. M. Duncan, and R. W. Vaughan, *J. Chem. Phys.*, 1979, **70**, 1219.

¹⁷ L. H. Dubois and G. A. Somorjai, *Surf. Sci.*, 1980, **91**, 514.

¹⁸ D. J. C. Yates, L. L. Murrell, and E. B. Prestridge, *J. Catal.*, 1979, **57**, 4.

¹⁹ T. M. Duncan, J. T. Yates, jun., and R. W. Vaughan, *J. Chem. Phys.*, 1980, **73**, 975.

cm^{-1}).²⁰ The latter are comparatively rare, but there are two other variations reported. In $[\text{HFe}_4(\text{CO})_{13}]^-$ (2), even in the absence of the π bond, the carbon atom would be bridging and again the oxygen atom is bonded to one metal.⁹ The carbon–oxygen stretching frequency of this group seems in doubt. The lowest frequency band is reported at 1723 cm^{-1} in a mull but 100 cm^{-1} higher in solution.²¹ The niobium trimer (3) contains a π -bonded carbonyl group that itself bridges two metal atoms.²² This CO bond is relatively long (1.30 \AA) and the carbonyl stretching frequency is very low (1330 cm^{-1}).

These bonding modes may be more difficult to detect in surface studies for two reasons. First, since the carbon–oxygen axis is not perpendicular to the metal surface, the component of the dipole-moment change normal to the metal, and therefore allowed by the surface selection rule, will be reduced. Secondly, the π -bonded groups have fairly low stretching frequencies that may be obscured by some supports. Interestingly though, photoelectron spectroscopy data on CO on a carbonized osmium surface has been interpreted in terms of a weak C—O bond, nearly parallel with the surface,²³ and also EELS spectra of CO in Ni(110) at low coverages exhibit a band at 1565 cm^{-1} .²⁴ This may be due to a π -bonded carbonyl and this particular surface contains potential sites similar to those shown in Figure 1. The observation of a π -bonded cyanide ligand in $(\text{NET}_4)[(\text{C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{CN})]$, acting in a similar manner to the π -carbonyl in (1), suggests this bonding may be available for a variety of π acid ligands.²⁵

Metal carbonyl clusters can stabilize a wide variety of organic moieties²⁶ and the binding modes established for two-carbon ligands are given in Figure 3. They can be used to provide reference spectra for chemisorbed hydrocarbons, but as yet detailed vibrational analyses of these species are relatively rare. EELS studies of acetylene and/or ethylene on Ni(111),^{27,28} Pt(111),²⁹ and Rh(111)³⁰ have been reported. Spectra of acetylene were observed on all three surfaces and are presented in Table 3. There are substantial differences in these spectra. This is particularly evident in the C–H stretching region. All show a marked lowering in these frequencies as compared with ν_1 of free acetylene (3374 cm^{-1}),³¹ indicating a change towards an alkene or alkane type of carbon atom. The four bonding modes shown in Figure 3b are all available to acetylene on these surfaces and it may be that the three surfaces do not use a common chemisorption site. There is reasonable agreement between the data on platinum with the analysed spectrum

²⁰ A. A. Pasynskii, Yu. V. Skripkin, J. L. Eremenko, V. T. Kalinnikov, C. G. Aleksandrov, V. G. Andrianov, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1979, **165**, 49.

²¹ K. Farmery, M. Kilher, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 1969, 2339.

²² W. A. Herrmann, M. L. Ziegler, K. Weidenhammer and H. Biersack, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 960.

²³ Y. Fukuda and J. W. Rabalais, *Chem. Phys. Lett.*, 1980, **76**, 47.

²⁴ J. C. Bertolini and B. Tardy, *Surf. Sci.*, 1981, **102**, 131.

²⁵ M. D. Curtis, H. R. Han, and W. M. Butler, *Inorg. Chem.*, 1980, **19**, 2096.

²⁶ A. J. Deeming, ref. 3, p. 391.

²⁷ J. E. Demuth and H. Ibach, *Surf. Sci.*, 1979, **85**, 365.

²⁸ J. E. Demuth and H. Ibach, *Surf. Sci.*, 1978, **78**, L238.

²⁹ H. Ibach and S. Lehwald, *J. Vac. Sci. Technol.*, 1978, **15**, 407.

³⁰ L. H. Dubois, D. G. Castner, and G. A. Somorjai, *J. Chem. Phys.*, 1980, **72**, 5234.

³¹ Y. Iwashita, F. Tamura, and A. Nakamura, *Inorg. Chem.*, 1969, **8**, 79.

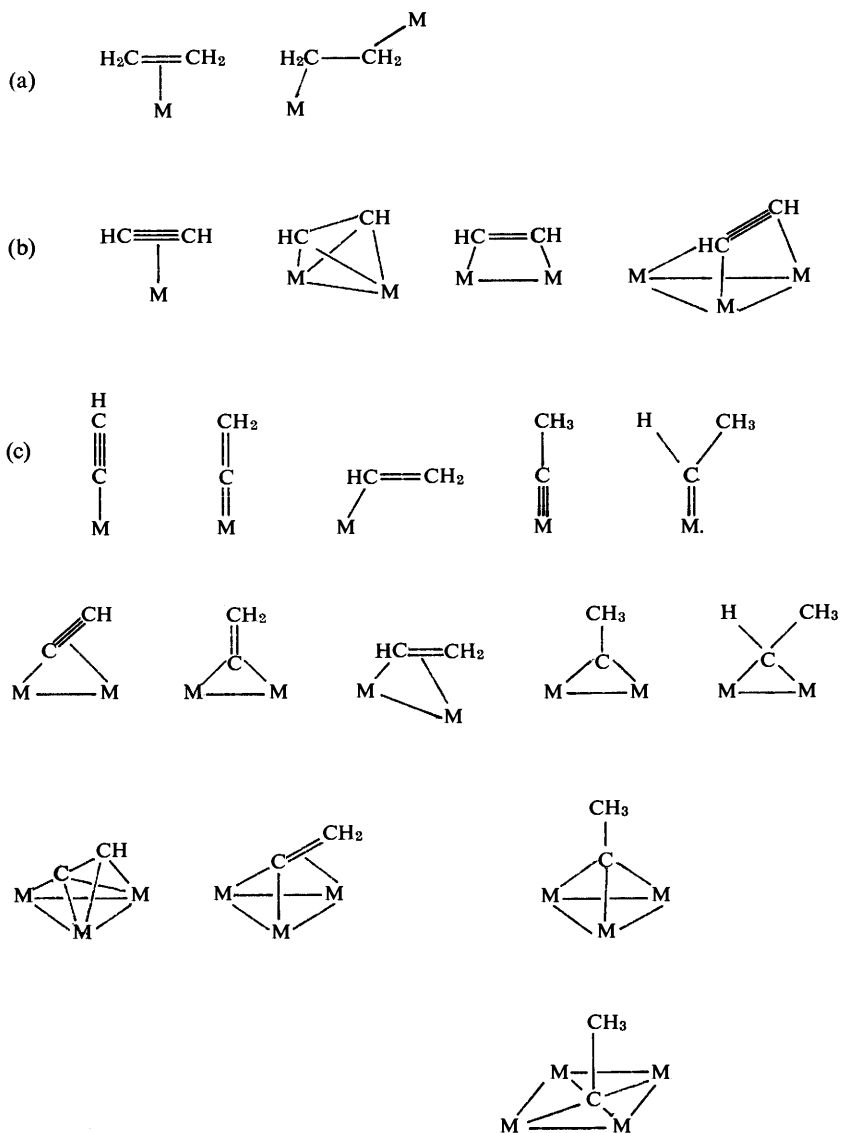
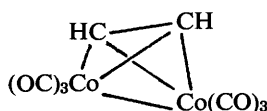


Figure 3 Co-ordination modes of C_2 hydrocarbon ligands in metal complexes: (a) ethylene, (b) acetylene, and (c) other fragments

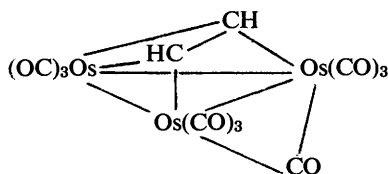
Table 3 Vibrational data of chemisorbed acetylene (frequencies in cm^{-1})

On Ni(111) ²⁷	On Rh(111) ³⁰	On Pt(111) ²⁹	$\text{C}_2\text{H}_2\text{CO}_2(\text{CO})_6$ ³¹	Assignment
2910	3085	3010	3113	ν_{CH}
1400	2984		3086	
1220		1310	1403	ν_{CC}
1065	887	985	894	δ_{CH}
870	706	770	768	
510	323	510	605	ν_{CM}
		340	551	

of $\text{C}_2\text{H}_2\text{CO}_2(\text{CO})_6$ (4),³¹ suggesting that form of edge bridging site is used on the 5d metal. A face bridging site is provided by $\text{Os}_3(\text{CO})_{10}(\text{C}_2\text{H}_2)$ (5)³² and this complex has markedly lower ν_{CH} frequencies (2989 and 2939 cm^{-1})³³ and are in



(4)



(5)

better agreement with the data on the nickel surface. EELS spectra of associatively adsorbed ethylene on Pt(111)^{29,34} and Ni(111)³⁴ have been observed at low temperatures. The only model complexes for which vibrational data are available are the π -bound systems shown in Figure 3a. Even so there can be significant variations in the spectra. For example, the three i.r. allowed ν_{CH} bands for ethylene under C_{2v} symmetry are at 3079, 3013, and 2988 cm^{-1} in Zeises salt, $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$,³⁵ but when complexed to an iron(0) centre, which will probably provide more back donation into the ethylene π^* orbital, these frequencies are lowered to 3020, 2970, and 2930 cm^{-1} [in $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$].³⁶ Allowing for these variations and the requirement that the observed bands should be polarized perpendicular to the metal surface, then the majority of the bands observed on these two metals fit chemisorbed molecular ethylene. Interestingly though a low frequency ν_{CH} was observed at 2690 cm^{-1} on the nickel surface, suggesting an additional binding mode. There are no exact model complexes for the 'di- σ '

³³ A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1975, 1614.

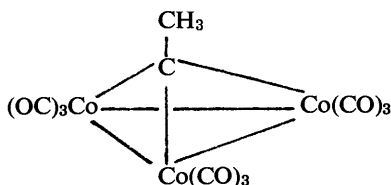
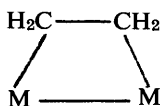
³⁴ J. Evans and G. S. McNulty, unpublished results.

³⁵ J. E. Demuth, H. Ibach, and S. Lehwald, *Phys. Rev. Lett.*, 1978, 40, 1044.

³⁶ J. Hiraishi, *Spectrochim. Acta*, 1969, 25, 749.

³⁷ D. C. Andrews and G. Davison, *J. Organomet. Chem.*, 1972, 35, 161.

bonded ethylene (6) proposed for the major site on silica-supported nickel and platinum and exhibit ν_{CH} bands in the region of 2780–2880 cm^{-1} ,³⁷ but a *trans* rotamer of $\mu(\text{CH}_2\text{CH}_2)[\text{Re}(\text{CO})_5]_2$ has been recently reported.³⁸



The vibrational data obtained for ethylene on Rh(111) from ~ 270 to 420 K were not in accord with simple adsorption (Table 4).³⁰ A new, partially dehydrogenated, species is formed that is also formed from acetylene and hydrogen and

Table 4 Comparison of the EELS data for the stable species observed for C_2H_4 on Pt and Rh(111) with *i.r.* and Raman spectra of model ethylidyne complexes (frequencies in cm^{-1})

Pt(111) ²⁹	Rh(111) ³⁰	$\text{Co}_3(\text{CO})_9\text{CCH}_3^{43}$	$\text{H}_3\text{Os}_3(\text{CO})_9\text{CCH}_3^{33}$	
3050w	3000w			
		2933	2916	$\nu(\text{CH})$ as
2920w	2900m	2892	2892	$\nu(\text{CH})$ s
1420sh	sh	1425	1438	$\delta(\text{CH}_3)$ as
1350s	1350s	1359	1367	$\delta(\text{CH}_3)$ s
1130s	1130s	1171	1147	$\nu(\text{CC})$
900w	880m	1008	1037	$\rho(\text{CH}_3)$
435w	450m	536,393		$\nu(\text{MC})$

appears to be analogous to the stable species observed for C_2H_4 on Pt(111).²⁹ The known geometries of ethynyl (C_2H), vinylidene (CCH_2), vinyl (CHCH_2), ethylidyne (CCH_3), and ethylidene (CHCH_3), moieties in metal complexes are shown in Figure 3c. Initially the EELS data were rationalized in terms of an ethylidene species, using CH_3CHCl_2 as the reference spectrum.²⁹ However, a subsequent interpretation of low energy electron diffraction (LEED) intensities favoured face bridging ethylidyne species with the C–C axis within 15° of normal to the metal surface.³⁹ This led to a reappraisal of the EELS data in terms of the new model, now using CH_3CBr_3 ⁴⁰ and $\text{CH}_3\text{CCO}_3(\text{CO})_9$ (7)⁴¹ as references. A

³⁷ B. A. Morrow and N. Sheppard, *Proc. R. Soc. London, Ser. A*, 1969, **311**, 391.

³⁸ B. Olgemöller and W. Beck, *Chem. Ber.*, 1981, **114**, 867.

³⁹ L. L. Kesmodel, L. H. Dubois, and G. A. Somorjai, *J. Chem. Phys.*, 1979, **70**, 2180.

⁴⁰ T. R. Stengle and R. C. Cooper, *J. Mol. Spectrosc.*, 1970, **34**, 33.

⁴¹ W. T. Dent, L. A. Duncanson, R. G. Guy, H. W. B. Reed, and B. L. Shaw, *Proc. Chem. Soc. London*, 1961, 169.

major problem in this comparison was that the strong band at 1130 cm^{-1} correlated with a CH_3 rocking vibration, which should be polarized parallel to the metal surface and therefore be very weak; this left the relatively weak band at 900 cm^{-1} as the $\nu(\text{C}-\text{C})$. On this basis, Demuth proposed a vinyl species using $\text{Sn}_2(\text{CH}=\text{CH}_2)_6$ as his reference.⁴² The geometry of this vinyl is not one found in cluster chemistry and is certainly quite unlike that of the tin complex. However, a normal co-ordinate analysis on the CH_3CCO_3 unit of (7) has shown that the original assignment of these two vibrations should be inverted and this gives a good fit with the surface species.⁴³ It must be stressed that the model complexes should be as close as possible to surface species. In this case, the frequencies of the two vibrations in question, $\nu_{\text{C}-\text{C}}$ and ρ_{CH_3} in the CH_3CX_3 species, are highly dependent upon the nature of the halide⁴⁰ and differ again from those observed on the cluster analogues. However, within a set of three ethylidyne complexes, (7), $\text{H}_3\text{Ru}_3(\text{CO})_9\text{CMe}$, and $\text{H}_3\text{Os}_3(\text{CO})_9\text{CMe}$, these variations are much less and so frequencies can be transferred to metal surfaces with more confidence. As shown in Table 4 the strong surface bonds can all correlate with the expected positions of the surface allowed $\text{C}-\text{CH}_3$ vibrations. The three weak features at ~ 3050 , ~ 1420 , and $\sim 900\text{ cm}^{-1}$, however, remain problematical. They may be due to an uncharacterized second-surface species.

While molecular acetylene and ethylene were observable on Ni(111) at 300 and 140 K, respectively, more vigorous conditions give rise to new EELS spectra. At room temperature, ethylene is apparently dissociated to acetylene.⁴⁴ High surface coverages of acetylene at $\sim 300\text{ K}$ have been variously described as causing trimerization to give benzene⁴⁵ and cleavage of the carbon-carbon bond;²⁸ very different spectra were reported indicating that the surface reactions are very sensitive to the conditions employed. At 450 K, the vibrational spectrum is quite simple (2980 m, 1300 vw, 790 s cm^{-1}). The two stronger bands were assigned to the $\nu(\text{CH})$ and $\delta(\text{CH})$ vibrations of a tilted bridging methine (CH) group. These modes have been observed at 3041 and 850 cm^{-1} , respectively, in $\text{Co}_3(\text{CO})_9\text{CH}$,⁴⁶ giving support to the C-C cleavage process.

From the discussion above, it is evident that organometallic complexes, including clusters, are a rich source of appropriate models for surface structures. One additional feature, not developed here but which has been reviewed recently,⁴⁷ is that these complexes exhibit many forms of non-rigidity. These include migration of CO and alkyne ligands over clusters, hydrides within the metal framework, and also rapid motions of the metal skeleton itself.

⁴² J. E. Demuth, *Surf. Sci.*, 1980, **93**, L82.

⁴³ P. Skinner, M. W. Howard, I. A. Oxtan, S. F. A. Kettle, D. B. Powell, and N. Sheppard *J. Chem. Soc., Faraday Trans. 2*, submitted for publication.

⁴⁴ J. C. Bertolini and J. Rousseau, *Surf. Sci.*, 1979, **83**, 531.

⁴⁵ J. C. Bertolini, J. Massardier, and G. Dalmay-Imelik, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 1720.

⁴⁶ M. W. Howard, S. F. A. Kettle, I. A. Oxtan, D. B. Powell, N. Sheppard, and P. Skinner, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 397.

⁴⁷ J. Evans, *Adv. Organomet. Chem.*, 1977, **16**, 319; E. Band and E. L. Muetterties, *Chem. Rev.*, 1978, **78**, 639; R. E. Benfield and B. F. G. Johnson, ref. 3, p. 471.

3 Clusters as Catalyst Sources

A. New Heterogeneous Catalysts.—A conventional preparation of a supported metal catalyst involves the introduction of a metal salt or co-ordination complex and subsequent reduction, normally by hydrogen at high temperatures. A wide variation of particle size distributions can be achieved by varying metal loadings and reaction conditions. This arises from competing kinetic processes, including the rate of reduction of the metal salt and the rate of metal migration and aggregation. Metal carbonyl clusters offer an alternative method of catalyst preparation since they contain preformed metal particles at, or near, a zero oxidation state. So interaction with an oxide support and thermal dissociation of some or all of the CO ligands could in principle give rise to a material that has a single metal particle size, and, by virtue of its unsaturation, be catalytically active. This more specific synthetic route would have dual advantages. First, since observations will be on a single metal species they can give more definite results and, secondly, these systems could be more specific in their activity.

The simplest preparative procedure is to interact a metal carbonyl with the oxide, dry the material, and then to heat it *in vacuo*. This follows through the sequence of initial physisorption, chemisorption, and further carbonyl dissociation. Methods of the initial interaction vary. One commonly used procedure is evaporation of the solvent from a suspension of a high surface area oxide in a solution of the carbonyl cluster in an organic solvent. While some physisorption probably occurs, this method will in many cases cause most of the complex to be in the form of crystallites. For example, the $\nu(\text{CO})$ i.r. bands of $\text{Os}_3(\text{CO})_{12}$ on silica gel agree well with those of the carbonyl as a nujol mull.⁴⁸ However, the i.r. spectra of $\text{Os}_3(\text{CO})_{12}$ in this region differ markedly between the solid and solution, primarily due to intermolecular coupling in the crystal lattice. So this result indicates that crystallites of $\text{Os}_3(\text{CO})_{12}$ are formed on silica gel. Evaporation of the *solution* must be avoided if simple physisorption of separated complex molecules is to be achieved.

Chemisorption could involve a variety of chemical reactions (Figure 4): (i) substitution of a carbonyl by a surface hydroxyl group, (ii) oxidative addition of the hydroxyl group, (iii) nucleophilic attack on the carbonyl carbon atom, and (iv) a Lewis acid interaction with a carbonyl oxygen atom (this is more likely for bridging groups). There is no compelling evidence for the first process at present. However, chemisorption of $\text{Os}_3(\text{CO})_{12}$ on silica involves loss of two carbonyl ligands and oxidative addition of a surface silanol group to afford (8).^{48,49} This species was characterized by comparing its $\nu(\text{CO})$ i.r. bands with those of a close analogue, $\text{HOs}_3(\text{CO})_{10}(\text{OSiPh}_3)$, and also by Extended X-Ray Absorption Fine Structure (EXAFS) measurements. This technique, which can give considerable structural information from amorphous as well as crystalline materials, is an

⁴⁸ A. K. Smith, B. Besson, J. M. Basset, R. Psaro, A. Fusi, and R. Ugo, *J. Organomet. Chem.*, 1980, **192**, C31.

⁴⁹ B. Besson, B. Morawek, A. K. Smith, J. M. Basset, R. Psaro, A. Fusi, and R. Ugo, *J. Chem. Soc., Chem. Commun.*, 1980, 569.

Relationship between Metal Carbonyl Clusters and Supported Metal Catalysts

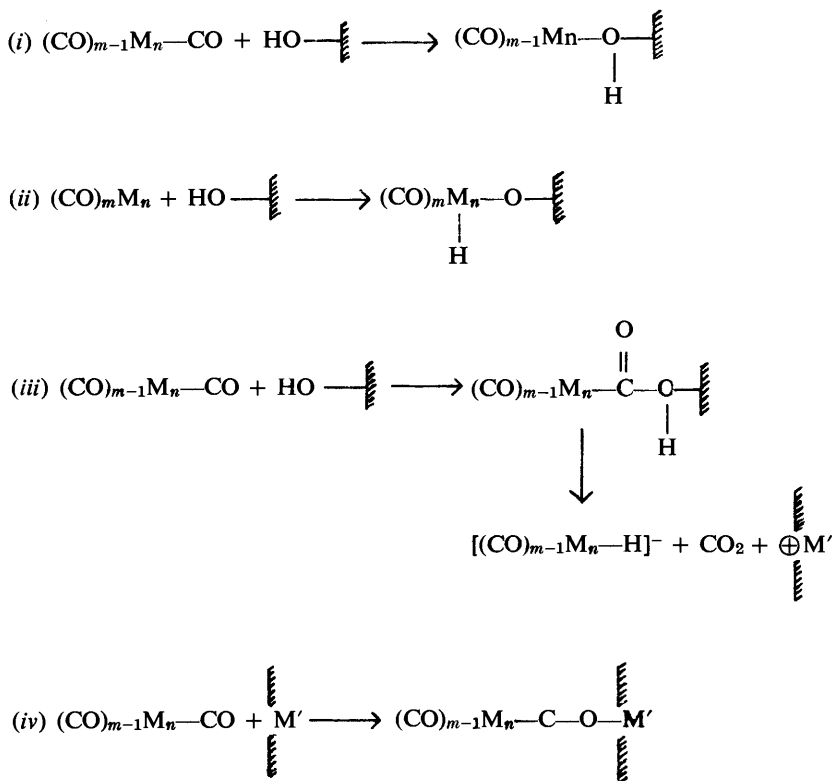


Figure 4 Possible chemisorption processes for a carbonyl cluster on an oxide surface: (i) substitution, (ii) oxidative addition, (iii) nucleophilic attack on the carbon atom, and (iv) Lewis acid interaction with the oxygen atom

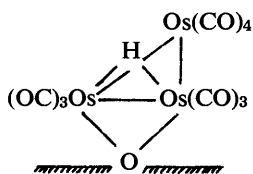
exciting prospect in this field. Similar species have been identified for $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ on several oxides.^{48,50} However, interaction of $\text{Fe}_3(\text{CO})_{12}$ and $\text{Fe}(\text{CO})_5$ with magnesia and η -alumina gives rise to $[\text{HFe}_3(\text{CO})_{11}]^-$ ionically bound to the surfaces.⁵¹ This anion is probably produced *via* nucleophilic attack by a surface hydroxyl group, and subsequent elimination of CO_2 , which probably forms an adsorbed carbonate. Finally, evidence for a Lewis acid binding has been obtained for $\text{Fe}_3(\text{CO})_{12}$ on a dehydrated HY type of zeolite.⁵² This is generally found by a lowering of the ν_{CO} frequency. Here this interaction is weak and may involve hydroxyl protons in the supercage. Interaction of $\text{MeMn}(\text{CO})_5$ with alumina produces a ν_{CO} band at 1510 cm^{-1} , and the i.r. evidence indicates that CO insertion had occurred rapidly to yield (9).⁵³

⁵⁰ J. Evans and B. P. Gracey, *J. Chem. Soc., Chem. Commun.*, 1980, 852.

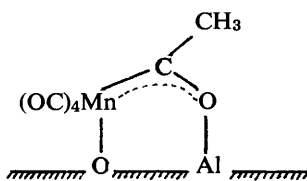
⁵¹ F. Hugues, A. K. Smith, Y. Ben Taarit, J. M. Basset, D. Commereuc, and Y. Chauvin, *J. Chem. Soc., Chem. Commun.*, 1980, 68.

⁵² D. Ballivet-Tkatchenko and G. Coudurier, *Inorg. Chem.*, 1979, **18**, 558.

⁵³ F. Correa, R. Nakamura, R. E. Stimson, R. L. Burwell, jun., and D. R. Schriver, *J. Am. Chem. Soc.*, 1980, **102**, 5112.

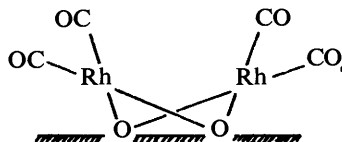


(8)



(9)

Nuclearity is not always maintained however. In the presence of oxygen, $\text{Rh}_4(\text{CO})_{12}$ produces $\text{Rh}^1(\text{CO})_2$ sites on silica.⁵⁴ The ν_{CO} bands in the infrared region indicated coupling between these metal centres, and the structure of this species has been assigned as (10).⁵⁵ The pyrolysis stages after initial chemi-



(10)

sorption also appear to cause nuclearity changes. In general, these pyrolysis products exhibit rather broad ν_{CO} bands in the infrared region and definite characterization is extremely difficult. However, it has been noted that the same species is formed on $\gamma\text{-Al}_2\text{O}_3$ from three different ruthenium clusters [$\text{Ru}_3(\text{CO})_{12}$, $\text{H}_4\text{Ru}_4(\text{CO})_{12}$, and $\text{Ru}_6\text{C}(\text{CO})_{17}$] after heating above 100°C ,⁵⁶ and a similar phenomenon was reported for osmium clusters at 200°C .⁴⁸ In both cases these were assigned as having $\text{M}^{\text{II}}(\text{CO})_2$ or 3 centres.

So the ideal situation of obtaining a controlled catalyst with a particular well established metal nuclearity is hard to attain. Nevertheless, as was shown by some of the earliest work in this area, partially decarbonylated species that are catalytically active can be generated.⁵⁷ Tracer studies were used to identify the stoichiometry of a butene isomerization, hydroisomerization, and hydrogenation catalyst formed from $\text{Ru}_3(\text{CO})_{12}$ and silica to be $\text{Ru}_3(\text{CO})_{\sim 5}$. The activity of this material did differ from that of ruthenium metal. The supported metals produced by complete thermal decomposition of metal carbonyls can differ from those prepared conventionally. For example, thermal activation of iron carbonyls

⁵⁴ A. Theolier, A. K. Smith, M. Leconte, J. M. Basset, G. M. Zanderighi, R. Psaro, and R. Ugo, *J. Organomet. Chem.*, 1980, **191**, 415.

⁵⁵ R. Whyman, ref. 3, p. 545.

⁵⁶ V. L. Kuznetsov, A. T. Bell, and Y. I. Yermakov, *J. Catal.*, 1980, **65**, 374.

⁵⁷ J. Robertson and G. Webb, *Proc. R. Soc. London, Ser. A*, 1974, **341**, 383.

on alumina under CO and H₂ give a small metal particle size of less than 20 Å.⁵⁸ So this is a valuable new method of preparing supported metal catalysts.

In general, low-oxidation-state metal carbonyls have relatively little affinity for oxygen-donating ligands. So functionalization of the oxide support with a soft donor ligand might help to maintain cluster nuclearity over a wider range of conditions. A second advantage is a much more substantial set of model complexes for reference spectra. A versatile anchoring method is to introduce a hydrolysable silyl group into the ligand, which can be used to react with surface hydroxyl groups (Figure 5a).^{59,60} Phosphines have been most commonly used and the results of some reactions are shown in Figure 5b. The success of a particular anchoring procedure is highly dependent upon the chemistry of the precursor. In some cases, notably Rh₄(CO)₁₂⁶⁸ and Rh₆(CO)₁₆,⁶¹ the cluster breaks down to give mononuclear Rh^I dicarbonyl sites. However, the frequencies of the ν_{CO} bands differ from those observed on unfunctionalized silica gel, indicating these rhodium centres are bound to a phosphine. A more common problem is that of a multiplicity of substitution products, illustrated by Ru₃(CO)₁₂.⁶² In general these can be identified by comparing the i.r. spectra with those of close analogues, but this can be difficult in practice because the i.r. bands tend to be broader on oxide surfaces than are those observed for model complexes in hydrocarbon solutions, and so overlap more. In some situations, the rates of stepwise carbonyl substitutions are sufficiently different that a single substitution product can be obtained, as is the case for Ru₆C(CO)₁₇⁶³ and substituted iridium carbonyl.⁶⁴ In these circumstances, the agreement of the i.r. spectra of the carbonyl stretching vibrations between anchored and model clusters, *e.g.*, Ru₆C(CO)₁₆(PPh₂C₂H₄SIL) and Ru₆C(CO)₁₆PPh₂Et, is very close, *i.e.*, within ~ 2 cm⁻¹. This increases the confidence in structural assignments and also indicates virtually no transmission of electronic effects from the support through the ligand chain to the cluster. This is in marked contrast to observations on clusters directly bonded to oxides. For example, the frequencies of the carbonyl vibrations of HO₃(CO)₁₀(OSiPh₃) and Os₃(CO)₁₂ on silica gel (8) differ by up to ~ 10 cm⁻¹. Electronic effects are transmitted through the cluster indicating that silica gel is a more electron-withdrawing ligand than is OSiPh₃, as would be expected. Substitution of a labile acetonitrile ligand and addition to an unsaturated cluster, as in (v) and (vi), allowed isolation of anchored osmium clusters from reactions under ambient conditions.⁶⁵⁻⁶⁷

⁵⁸ D. Commereuc, Y. Chauvin, F. Hugues, J. M. Basset, and D. Oliver, *J. Chem. Soc., Chem. Commun.*, 1980, 154.

⁵⁹ K. G. Allum, R. D. Hancock, I. V. Howell, S. McKenzie, R. C. Pitkethly, and P. J. Robinson, *J. Organomet. Chem.*, 1975, **87**, 203.

⁶⁰ R. L. Burwell, *Chem. Technol.*, 1974, **4**, 370.

⁶¹ H. Knözinger, E. W. Thornton, and M. Wolf, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 1888.

⁶² S. C. Brown and J. Evans, unpublished results.

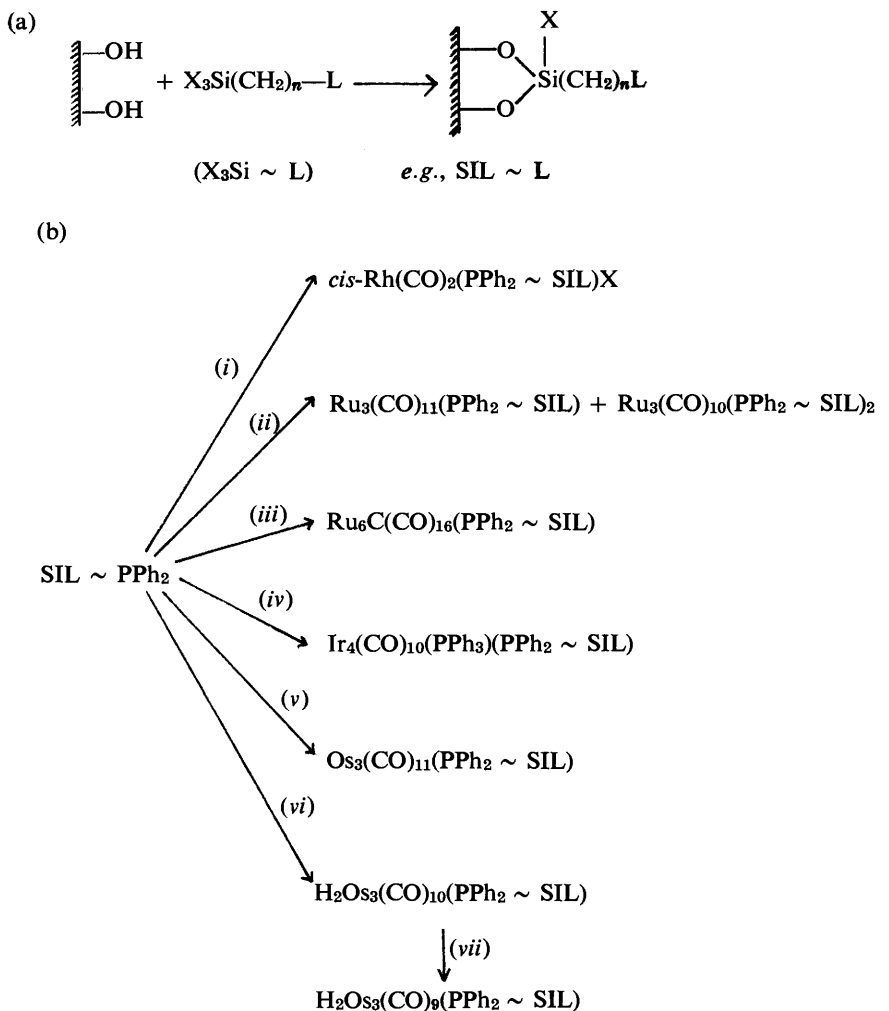
⁶³ S. C. Brown, J. Evans, and M. Webster, *J. Chem. Soc., Dalton Trans.*, to be published.

⁶⁴ T. Catrillo, H. Knözinger, J. Leito, and M. Wolf, *Inorg. Chim. Acta.*, 1980, **44**, L239.

⁶⁵ S. C. Brown and J. Evans, *J. Chem. Soc., Chem. Commun.*, 1978, 1063.

⁶⁶ R. Pierantozzi, K. J. McQuade, B. C. Gates, M. Wolf, H. Knözinger, and W. Ruhmann, *J. Am. Chem. Soc.*, 1979, **101**, 5436.

⁶⁷ B. C. Gates and J. Leito, *Chem. Technol.*, 1980, 195 and 248.



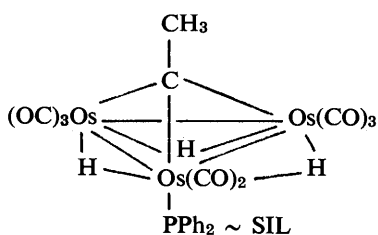
(i) $\text{Rh}_6(\text{CO})_{16}$ ⁶¹; (ii) $\text{Ru}_3(\text{CO})_{12}$ ⁶²; (iii) $\text{Ru}_6\text{C}(\text{CO})_{17}$ ⁶³; (iv) $\text{Ir}_4(\text{CO})_{11}(\text{PPh}_3)$ ⁶⁴; (v) $\text{Os}_3(\text{CO})_{11}$ -
(MeCN)⁶⁵; (vi) $\text{H}_2\text{Os}_3(\text{CO})_{10}$; (vii) heat⁶⁶⁻⁶⁷

Figure 5 (a) Generalized functionalization of oxides, (b) some reactions of phosphinated silica gel

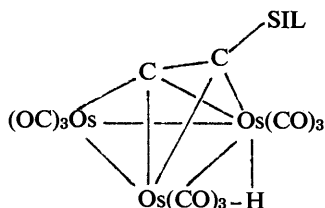
The chemistry of clusters anchored to phosphine functionalized oxides has been restricted to investigations of their thermal stability and some catalytic studies. $\text{H}_2\text{Os}_3(\text{CO})_9(\text{PPh}_2 \sim \text{SIL})$ and $\text{HAuOs}_3(\text{CO})_{10}(\text{PPh}_2 \sim \text{SIL})$ have been reported to catalyze but-1-ene isomerization.⁶⁶ The former material and $\text{Os}_3(\text{CO})_{11}$ -

($\text{PPh}_2 \sim \text{SIL}$) also catalyse ethylene hydrogenation, albeit slowly.^{68,69} Indeed the anchored complexes have lower turnover rates than their dissolved analogues under similar conditions. This may partly be due simply to having a third phase present, but i.r. studies demonstrated that the appended catalysts were being deactivated in two ways. One parallels the solution chemistry in which the ethylene is metallated and provides the ethylidyne ligand in (11). The second is specific to the oxide surface and appears to yield osmium(II) carbonyl sites bound to a phosphine ligand. More active olefin hydrogenation catalysts are provided by $\text{Ru}_6\text{C}(\text{CO})_{17}$ ⁶⁸ and rhodium carbonyls⁷⁰ on functionalized silicas, but in each case aggregation to the metal ensued; 12–15 Å rhodium particles were identified in the latter study. It is interesting that the amine functionalization hindered aggregation more.

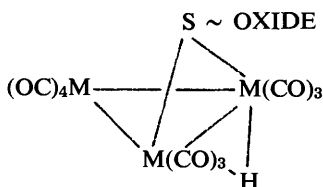
So although simple pendant ligands may retard the drawbacks of direct interaction between oxides and cluster complexes, *viz.*, cluster breakdown and aggregation to metals, they are not prevented. Attempts to overcome this problem are currently under way using bridging and polydentate anchoring ligands. The first such species reported was (12), which incorporates a face bridging acetylide.⁶⁶ More recently, ruthenium and osmium trinuclear complexes



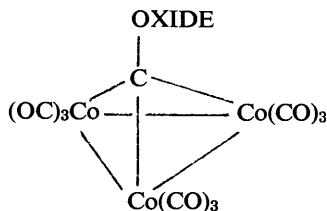
(11)



(12)



(13) M = Ru, Os



(14)

⁶⁸ S. C. Brown and J. Evans, *J. Mol. Catal.*, 1981, 11, 143.

⁶⁹ S. C. Brown and J. Evans, *J. Organomet. Chem.*, 1980, 194, C53.

⁷⁰ E. W. Thornton, H. Knözinger, B. Tesche, J. J. Rafalko, and B. C. Gates, *J. Catal.*, 1980, 62, 117.

have been anchored on pendant thiolates (13)^{50,71} and tricobalt carbon complexes (14) have been immobilized;⁵⁰ these procedures were also generalized to other oxides. The osmium derivatives of (13) are particularly stable and synthetic chemistry has been performed on them.⁷² Oxidation of one carbonyl group by Me₂NO in the presence of acetonitrile has afforded HO₂S₃(CO)₉(MeCN)(S~OXIDE) on silica and alumina. The acetonitrile ligand can be readily substituted and thus forms an incipient vacant site, giving the complex more potential for catalytic activity. Interestingly, HO₂S₃(CO)₉(MeCN)(SPrⁿ) catalyses pentene isomerization under conditions in which HO₂S₃(CO)₁₀(SPrⁿ) is inactive.

It is apparent that the ideal of a durable active heterogeneous catalyst with a single cluster species is not trivial to attain. Direct interaction and anchoring with monodentate ligands do not seem appropriate. However, use of bridging and polydentate ligands, such as HC(PPh₃)₃, which co-ordinates over a face of the rhodium tetrahedron in Rh₄(CO)₉[HC(PPh₃)₃],⁷³ may well increase the resistance to fragmentation sufficiently to achieve this goal.

B. Synthesis Gas Chemistry.—The impetus for this work is to provide processes for petrochemical synthesis from a synthesis gas, which could be coal-based.⁷⁴ Presently, most synthesis gas is derived from methane and other petroleum products and is mainly used for conversion to hydrogen *via* the water gas shift reaction, for ammonia manufacture, and also methanol manufacture.^{74,75} The viability of converting a particular process to a coal base is dependent upon the economic and political climate in different countries. It has been suggested that one of the first processes to convert in the USA would be the manufacture of ethylene-derived oxygenates (ethylene glycol) and this could be attractive in 6—14 years.⁷⁴ However, in 1978, outside Eastern Europe, there were 18 Lurgi gasifiers operating for the production of synthetic natural gas (SNG: 26—32% CO₂, 17—21% CO, 36—43% H₂, and 8—13% CH₄).⁷⁶ Thirteen of these were in Sasolburg (South Africa) and a further 40 are planned there by 1981, increasing the capacity by *ca.* 42 Mm³ per day. The majority of the synthesis gas produced was used to manufacture 1.5 Mton of gasoline per year,⁷⁷ using two processes with iron catalysts. About 6000 tons of coal per day were used for the gasifiers with an additional 5400 tons of coal per day used in the direct production of electricity and steam for the synthesis project. The extended capacity will consume *ca.* 40 000 tons of coal per day. The scale of such operations causes problems of site,^{74,78} but even so a pilot plant for coal liquefaction has been operating in

⁷¹ T. Catrillo, H. Knözinger, and M. Wolf, *Inorg. Chim. Acta.*, 1980, **45**, L235.

⁷² J. Evans and B. P. Gracey, unpublished results.

⁷³ A. A. Arduani, A. A. Bahsoun, J. A. Osborn, and C. Voekler, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 1024.

⁷⁴ J. E. Johnson, *Chem. Technol.*, 1981, 44.

⁷⁵ C. M. Bartish and G. M. Drissel, *Kirk-Othmer Encycl. Chem. Technol.*, 3rd Ed., 1978, **4**, 772.

⁷⁶ J. Huebler, and J. C. Janka, *Kirk-Othmer Encycl. Chem. Technol.*, 3rd Ed., 1980, **11**, 410.

⁷⁷ C. D. Kalfadelis and H. Shaw, *Kirk-Othmer Encycl. Chem. Technol.*, 3rd Ed., 1980, **11**, 447.

⁷⁸ J. Elkington, *The Guardian*, 26th March, 1981.

West Germany and another is planned for North Wales to go on stream in 1984.⁷⁸

The chemical interest, however, is in the design of specific catalysts. Efficient catalysts, based on zinc-copper-alumina, already operate for methanol manufacture.⁷⁵ Indeed, dehydration of methanol using 'shape selective' zeolites, e.g. ZSM-5,⁷⁹ is an alternative route to synthetic gasoline.⁸⁰ Mobil's process gives a relatively narrow molecular-weight range with less than 3% methane and ending by $\sim C_{11}$.

On the basis of two surveys of metal carbonyl catalyst precursors, one below 200 atm and 200 °C⁸¹ and another at 2000 atm and 230 °C,⁸² it appears that Co, Ru, Rh, Ir, and Pt complexes form the most active catalysts for synthesis gas conversion. Activity appears to be strongly solvent dependent and we shall discuss results obtained on the first three elements, which seem to have most potential at this stage.

Reports on three studies in which $Co_2(CO)_8$ was used as a precursor have been published;⁸¹⁻⁸³ different reaction conditions were used in each study. In all cases, liquid products predominated. At 200 °C, under an initial pressure of 130 atm ($CO:H_2 = 1:1$) in glyme or diglyme, then the major product from synthesis gas was ethanol (80%).⁸¹ Under a higher pressure (300 atm) and in benzene, heptane, and *p*-dioxan, the major products were methanol and methyl formate.⁸³ Rates were solvent dependent (*p*-dioxan > benzene > heptane) and in the ether solvent ethanol and propanol were also detected and shown to be secondary products from methanol. At 230 °C and 2000 atm, rates were faster in toluene than in *N*-methylpyrrolidone (NMP), with ethylene glycol (25%) as an additional product to methanol (31%) and methyl formate (35%).⁸² These conditions approach those presented 30 years ago for the synthesis of ethylene glycol, glycerol, and their esters and ethers.⁸³ $Co(OAc)_2$ was a typical catalyst precursor at pressures of ~ 3000 atm.⁸⁴ Samples obtained after the pressure was released indicate that $HCo(CO)_4$ was the principal (or only) cobalt-containing species in solution in the 300 atm and 2000 atm studies. The cobalt chemistry evident from the recovered solutions from the 200 atm reactions is complex.⁸¹ Diglyme solutions that have operated between 120 and 180 °C are red-brown and exhibit i.r. bands that were assigned to $Co_2(CO)_8$, $[(diglyme)_nCo][Co(CO)_4]_3$, and an unusual polynuclear complex (15). However, after operation at 200 °C, these solutions are yellow and exhibit no $\nu(CO)$ i.r. bands attributable to metal carbonyls.

⁷⁸ M. S. Spencer and T. V. Whittam in 'Catalysis', ed. C. Kemball and D. A. Dowden (Specialist Periodical Reports), The Chemical Society, London, 1980, Vol. 3, p. 189.

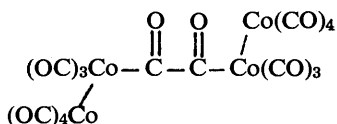
⁸⁰ S. L. Meisel, J. P. McCullough, C. H. Lechthaler, and P. B. Weisz, *Chem. Technol.*, 1976, 86.

⁸¹ R. J. Daroda, J. R. Blackborow, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1980, 1098.

⁸² W. Keim, M. Berger, and J. Schlupp, *J. Catal.*, 1980, **61**, 359.

⁸³ J. W. Rathke and H. M. Feder, *J. Am. Chem. Soc.*, 1980, **102**, 3625.

⁸⁴ W. G. Gresham, B. P. 655 237, 1951 (*Chem. Abstr.*, 1952, **46**, 7 115h); B.P. 665 698, 1952, U.S.P. 2 623 906, 1952 (*Chem. Abstr.*, 1952, **46**, 11 232f).



(15)

Methanol and methyl formate have been identified as major reaction products from $\text{Ru}_3(\text{CO})_{12}$ -initiated catalyses under a variety of conditions, although again, actual product distributions were sensitive to solvent and conditions.^{81,82,85} Little gas uptake was noted at 200 °C, under 300 atm in glyme solvents, but catalysis was evident in 2-methoxyethanol under 100 atm of synthesis gas at 170 °C.⁸¹ No metal carbonyls were observed in the recovered solutions; an alkoxide gel was present. Apparent Fischer-Tropsch catalysis by $\text{Ru}_3(\text{CO})_{12}$ under 100 atm at ~ 300 °C in heptane has been shown to be a heterogeneous reaction that is only apparent after the carbonyl starts to decompose to ruthenium metal.⁸⁶ After ~ 1 day, all the carbonyl is decomposed. Studies in THF solution indicated that the fate of the ruthenium is strongly pressure dependent.⁸⁵ Hydrogenation of carbon monoxide proceeds at 1300 atm and 225–275 °C to give > 99% methanol and methyl formate. A variety of catalyst precursors, *e.g.*, $\text{Ru}_3(\text{CO})_{12}$, $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$, and $\text{Ru}(\text{acac})_3$, gave similar results and the i.r. spectra of samples extracted from working solutions show only the ruthenium to be in the form of $\text{Ru}(\text{CO})_5$. Under milder conditions (80 °C and 135 atm of synthesis gas) the pentacarbonyl and $\text{Ru}_3(\text{CO})_{12}$ are present in approximately equal concentrations, but increasing the temperature without markedly raising the gas pressure promotes decomposition to the metal. It is interesting that under conditions of mixed homogeneous and heterogeneous catalysis, methanol formation decreased with decreasing $\text{Ru}(\text{CO})_5$ concentration. $\text{Ru}(\text{CO})_5$ has also been detected after, *and during*, synthesis gas conversion, in under ~ 340 atm of CO and H_2 and ~ 200 °C in acetic acid solution.⁸⁷ Again a variety of precursors gave equivalent results. Methyl acetate and ethylene glycol diacetate were the major products. The rate of production of the latter is strongly related to the concentration of carboxylic acids. Partial pressure dependences of H_2 and CO favoured involvement of $\text{H}_2\text{Ru}(\text{CO})_4$.

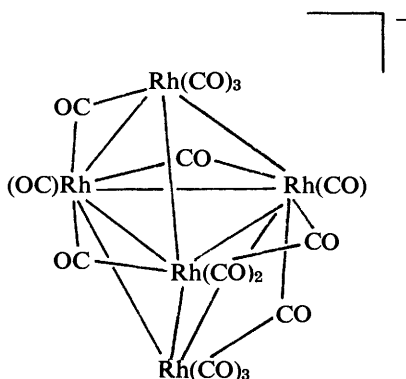
There is obvious difficulty in ascribing these catalytic activities to particular species. In none of these cases do clusters appear to be the active species. *In situ* i.r. monitoring of the ruthenium system gives good evidence for the involvement of mononuclear carbonyl complexes. This method has also been employed on rhodium-catalysed systems, where there is evidence for cluster catalysis. A variety of rhodium carbonyls including $\text{Rh}(\text{CO})_2(\text{acac})$ can be used as precursors for the

⁸⁵ J. S. Bradley, *J. Am. Chem. Soc.*, 1979, **101**, 7419.

⁸⁶ M. J. Doyle, A. J. Kouwenhoven, C. A. Schapp, and B. van Oort, *J. Organomet. Chem.*, 1979, **174**, C55.

⁸⁷ B. D. Dombek, *J. Am. Chem. Soc.*, 1980, **102**, 6855.

catalytic synthesis of ethylene glycol and other polyhydric alcohols.⁸⁸ *In situ* i.r. studies have been reported on these systems at pressures of up to 1000 atm, somewhat lower than some of the optimum catalytic conditions.⁸⁹ In the presence of amines and/or alkali-metal carboxylates, solutions of $\text{Rh}(\text{CO})_2(\text{acac})$ in tetraglyme or sulfolane, when treated with 1000 atm of CO/H_2 (1:1) at temperatures below 180 °C, give i.r. bands indicative of $[\text{Rh}_5(\text{CO})_{15}]^-$ (16)⁹⁰ and



(16)

$[\text{Rh}(\text{CO})_4]^-$; other clusters, *e.g.*, $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$, behaved similarly. At higher temperatures (~ 250 °C) more approaching optimum catalytic conditions for polyol formation, higher nuclearity cluster complexes (Rh_{13-15}) are evident. Three clusters containing encapsulated atoms, $[\text{Rh}_6(\text{CO})_{16}\text{C}]^{2-}$, $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$, and $[\text{Rh}_{17}(\text{S}_2)_2(\text{CO})_{32}]^{3-}$, show increasing stability and are active catalysts under conditions in which they are the only detectable species. Although they are less active than $\text{Rh}(\text{CO})_2(\text{acac})$ -based systems (by a factor of 2—10), they represent the most probable examples of catalysis by clusters. Studies of this type represent one of the most effective ways of investigating these systems, when linked to conventional mechanistic methods. A very recent report has demonstrated the applicability of ^{13}C n.m.r. to studying high-pressure reactions, potentially a very powerful technique.⁹¹ Intermolecular exchange even under 1000 bar of CO/H_2 (2.1:1) was sufficiently slow to allow clear observation of the spectra due to the dissolved complexes. These clearly showed the conversion of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ to $[\text{Rh}_5(\text{CO})_{15}]^-$ at room temperature. At low temperatures (~ -50 °C) this transformation is slow.

⁸⁸ R. L. Pruett and W. E. Walker, U.S.P. 3 833 634, 1974 (*Chem. Abstr.*, 1973, 79, 78 081).

⁸⁹ J. L. Vidal and W. E. Walker, *Inorg. Chem.*, 1980, 19, 896.

⁹⁰ A. Fumagilli, T. F. Koetzle, F. Takusagawa, P. Chini, S. Martinengo, and B. T. Heaton, *J. Am. Chem. Soc.*, 1980, 102, 1740.

⁹¹ B. T. Heaton, J. Jonas, T. Eguchi, and G. A. Hoffman, *J. Chem. Soc., Chem. Commun.*, 1981, 331.

Synthesis gas conversion has also been effected by materials formed by the deposition of polynuclear rhodium carbonyls on a variety of oxides, followed by pyrolysis *in vacuo* or under hydrogen.⁹² Although these catalysts are not well characterized, they show interesting facets. First, these reactions were carried out under relatively mild conditions, 205–225 °C and 65 Torr of CO/H₂ (~ 1:2). Secondly, the product distributions were support dependent. While methane was predominant on acidic supports, *e.g.*, SiO₂, ethanol was the major product on more neutral oxides, *e.g.*, La₂O₃ and TiO₂, and methanol predominated on basic supports, *e.g.*, MgO. Thirdly, on La₂O₃, the percentage of ethanol formed varied within the range of 29–61 % for different complexes under similar conditions $\{(C_5H_5)_2Rh_2(CO)_3 < Rh_4(CO)_{12} > Rh_6(CO)_{16} > (NEt_4)_3[Rh_7(CO)_{16}] > [NBu_4]_2[Rh_{13}(CO)_{23}H_3]\}$. This ethanol selectivity was substantially greater than a conventional heterogeneous rhodium catalyst (17% ethanol). Pyrolysis of Fe₃(CO)₁₂ on oxides such as MgO and Al₂O₃ also produces Fischer–Tropsch catalysts with unusual selectivities.^{58,93} At 176 °C, after 1% CO conversion, propene was the major product (32%), with methane (26%) also being formed in reasonable quantities. The catalyst has very small metal particles initially (< 20 Å) but these increase to 200–500 Å by the end of the run. The selectivity for propene drops concomitantly, indicating a unique process for the smaller particles. Exposure of a freshly prepared catalyst to ethylene also yields propene as the major product. This suggests that methylene groups are formed on the iron surface. Hydrogenation can then afford methane, and further reaction with ethylene to form a metallocyclobutane is a possible route towards propene. Finally, highly active methanation catalysts have been prepared by supporting Mo(CO)₆ and W(CO)₆ on alumina.⁹⁴ Initially, these materials appear to contain adsorbed ‘sub-carbonyl’ mononuclear species [M(CO)₅ or M(CO)₃] and possibly the activity may be due to these centres.

4 Conclusions

Surface science and cluster chemistry are both rapidly developing fields, and so conclusions about their relationships may change in the next few years. However, it seems that clusters have a valid contribution to make as models for metal surfaces. This approach has its limitations; a structure or mechanism determined on a homogeneous system is in no way binding to a heterogeneous one. In the author's view the most incisive contribution cluster chemistry can make is to form a bank of spectroscopic data on well defined systems. Work on clusters as catalyst sources is in its early stages, particularly in heterogeneous systems. Nevertheless some results, even though they are not yet well understood, seem promising. Recent spectroscopic developments offer exciting extensions to the situation five or so years ago. These include Fourier transform infrared (with greatly increased sensitivity, particularly in the far i.r.), high-resolution solid-

⁹² M. Ichikawa, *J. Chem. Soc., Chem. Commun.*, 1978, 566; *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2268 and 2273.

⁹³ F. Hugues, B. Besson, and J. M. Basset, *J. Chem. Soc., Chem. Commun.*, 1980, 719.

⁹⁴ A. Brenner and D. A. Hucul, *J. Am. Chem. Soc.*, 1980, **102**, 2482.

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state n.m.r. (using magic angle sample spinning and multiple-pulse sequences), and EXAFS. These methods offer the promise of greatly improving the degree of characterization of heterogeneous systems, and used in combination can increase this near to the level currently expected for solution studies.

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