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Author

Muetterties, E.L.

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E. L. Muetterties, J. C. Hemminger, and
G. A. Somorjai

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A Coordination Chemistry Guide to Structural Studies of Chemisorbed Molecules

by

E. L. Muetterties,* J. C. Hemminger and G. A. Somorjai

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
Department of Chemistry,University of California,
Berkeley, California 94720

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*Department of Chemistry, Cornell University, Ithaca, New York 14853

A Coordination Chemistry Guide to Structural Studies of Chemisorbed Molecules

Sir:

An understanding of surface chemistry at the molecular level in the context of the chemisorbed state and of the dynamic processes of corrosion, adhesion and catalysis represents a major scientific challenge.[1,2] Such a "molecular" understanding requires as a first step the delineation of the structure of the molecules, atoms or groups of atoms chemisorbed at the surface; the issues of bonding and dynamic chemistry cannot be properly examined without such structural information. Surface crystallography, based on the interpretation of low-energy electron diffraction (LEED)[2,3] data, can rigorously define the simplest and ideal case of an ordered chemisorption of atoms[4] on a single crystal but requires supplementary information for an accurate structural analysis of more complex chemisorbed species. It is the purpose of this article to describe a simple supplementary structural technique which is based on a known, but not exploited, surface reaction, the displacement reaction.[5] In addition, a convention is proposed for the notation or description of chemisorbed states wherein there is some unification of surface chemistry and inorganic terms so as to facilitate communication through such interfaces as inorganic and surface science and homogeneous and heterogeneous catalysis.

Before discussing displacement reactions at metal surfaces,[6] it is essential to describe the various classes of chemisorbed states for molecules. At very low temperatures, <100 K, the chemisorption process is in all cases associative (no fragmentation or rearrangement of the molecule); however, this elementary step may be followed by processes other than reversible desorption as the temperature is raised and it is these processes that occur above 200K that are of primary interest.

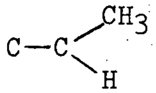
In the simplest case of chemisorption, a molecular associative step is the only process that occurs from very low metal surface temperatures to some higher temperature where a desorption step occurs. This limiting case, Class 1, of fully reversibly molecular associative chemisorption may have the notation mA_R, mA for molecular associative[7] and subscript R for thermally reversible. Molecules that display this type of chemisorption behavior are carbon monoxide on nickel and platinum[8] and acetonitrile on nickel (111).[9] In these examples, only one atom of the molecule is within bonding distance of metal atoms and may be described as an η^1 ligand following the <u>hapto</u> notation of Cotton,[10] i.e. mA_R-η^1. Metal atom connexity with respect to the donor atom of the molecule could be specified,[10] e.g. mA_R-$\eta^1\mu_2$ for a CO bridge bonded between 2 metal atoms. In contrast, to the CO and CH_3CN examples, the reversible chemisorption of ethylene on copper[11] probably involves a bonding approach of both carbon atoms to the metal surface atom(s) and could be differentiated by the notation, mA_R-η^2.

An alternative sequence for a chemisorption process would be an initial molecular associative adsorption followed by a dissociative reaction step at some higher temperature and then reversible molecular desorption at a still higher temperature. This process, Class 2, would be molecular dissociative and reversible, mD_R. Typical molecules that exhibit such behavior are the diatomics like hydrogen, nitrogen (on some metals) and cyanogen,[12] the heavier halogens and oxygen on the more noble metals. Closely related to Class 2 is a molecular dissociatve chemisorption which, on thermal desorption,[13] yields a relatively clean surface and a set of gaseous desorption products that are not reactants. This Class 3 process would be typical of the behavior of HX (X = I and CN) on the noble metals with H_2 and X_2 desorbed from the surface at different temperatures. To distinguish this class from a fully irreversible chemisorption, the notation mD_I-M_R could be used since a "clean" metal (M) surface is regenerated (subscript R). Classes 2 and 3 are analogous to oxidative addition reactions in coordination chemistry.

The fourth class of chemisorption is molecular dissociative and completely irreversible, mD_I. For this class, neither the original molecule nor a clean metal surface is formed on flash heating of the crystal. Hydrocarbons, e.g. ethylene on tungsten, commonly show this type of chemisorption behavior. The fifth and sixth classes comprise associative and dissociative polymerization, mAP and mDP, of a molecule and of a molecular fragment, respectively. Possible examples are $(CN)_2$ and HCN to yield chemisorbed $(C_2N_2)_x$ and $\dashv(CN)\vdash_3$.

In addition to the above six general classes of chemisorption processes, we cite three important classes of chemisorption *states* that require discussion because their behavior in surface displacement reactions will be distinctive: (1) an mARH state in which the molecule has undergone substantial rehybridization; (2) an mAR state in which the molecule has rearranged to a new molecule; and (3) an mARF state in which the molecule has rearranged to a molecular *fragment*. These classes may be illustrated with the *hypothetical* case of propyne chemisorption on metal surfaces. Propyne initially could chemisorb in mA-η^1 form with the conventional σ-π interaction with the surface. At higher temperatures, there could be a rehybridization of the π system so that each acetylenic carbon atom forms relatively strong σ bonds to at least two metal atoms as illustrated in **1**:

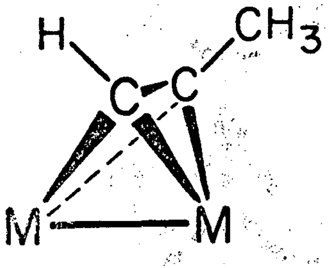
1

This type of bonding interaction wherein the acetylene (typically a disubstituted acetylene) ligand has become formally a four electron donor molecule is common in dinuclear-[14-17] and cluster-[17,18] acetylene chemistry. Alternatively, the propyne, through a hydrogen atom migration could rearrange to give a bound allene molecule and this would be an mAR state. The third possibility is rearrangement to a bound  $C{-}C\begin{smallmatrix}CH_3\\ H\end{smallmatrix}$ fragment and this would be an mARF state. In fact, the bound C_2H_2 in a molecular osmium cluster,[19] $H_2Os_3(CO)_9C_2H_2$, is a fragment as partially illustrated in **2** although the C_2H_2 species bound in two dinuclear complexes[15,16] is

2

HCCH and the binding is as shown in **1**.

Now we address the issue of utilizing the surface displacement reaction to obtain supplementary structural information. The ultra high vacuum system developed by surface scientists should be minimally equipped for Auger, LEED, mass spectroscopy, and perhaps photoelectron experiments and with an isolation cell for the metal crystal.[20] Key experiments for the displacement reactions



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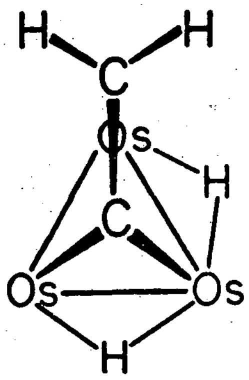

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are mass spectroscopic monitoring of the displacement reaction[21] and Auger analysis of the surface after reaction.[22] Essential to a meaningful Auger analysis is the use of a displacing molecule that has an element not found in the initially chemisorbed molecule, e.g. the use of CH_3NC to displace CO or CO to displace CH_3CN.[22]

To a first approximation, the surface of a transition metal has a chemistry similar to a zerovalent molecular or cluster complex of that metal, albeit a very reactive complex.[17,23] Fortunately, the extensive, classical studies of displacement reactions in coordination chemistry[24] and recent systematic calorimetric studies[25] of these reactions provide a logical base for selection of reactant molecules in displacement reactions on metal surfaces.

If a molecule is bound to a surface in an mA-η^x state in which no rearrangement or extensive rehybridization of the molecule has occurred, then it should be possible to displace the molecule by another which is a stronger field ligand.[24a,b] Thus acetonitrile, a weak field ligand, should be readily displaceable. We have found that this molecule shows mA_R chemisorption on Ni(111) and facile displacement by CO at 300 K.[9] In coordination complexes, olefins and acetylenes bound in the conventional η^2 form are typically less strongly bound than CO[25] and are displaceable by CO; facile displacement of an olefin or an acetylene from a surface by CO would be strong evidence for an η^2 binding state. Water, alcohols and ammonia are weak field ligands[24a] and should be readily displaced from a metal surface by CO. If facile displacement is not observed, this would be a strong indication of a molecular dissociative chemisorption for these molecules since CO would not displace O, OH, OR or NH_2. In this case, reaction of the surface with HCN could lead to desorption of the original molecules because CN is a far stronger field ligand than OH, OR or NH_2.

In a set of displacement reactions, it is essential that the initial molecule be chemisorbed to less than full monolayer coverage. At full monolayer coverage, the chemisorbed surface is formally analogous to the coordinately saturated coordination complex or cluster which often exhibits a relatively high activation energy for ligand exchange or displacement reactions. If a molecule is very strongly π bonded to a metal surface, cyanogen[12] may be an effective displacement molecule since $(CN)_2$ may exhibit dissociative chemisorption to give a bound CN species with extensive surface oxidation[26] because of electron transfer to CN(CN^-). A more general alternative to cyanogen is iodine.[27]

A molecule exhibiting mA chemisorption and providing two electrons to the surface bound state may be within bonding distance of one, two, three or four metal atoms as in the established surface and cluster chemistry of carbon monoxide, i.e. CO terminally bound to one metal atom or bridge bonded to two or more metal atoms.[17,23] Theoretical[28] and experimental[25] evidence suggests that there is little energy difference between these states. Hence, we do not anticipate that displacement reactions can provide this type of structural information although LEED and vibrational spectroscopy can.

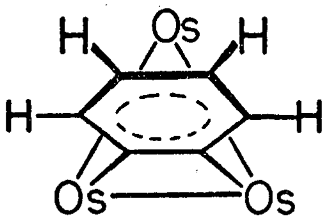
In contrast to the above case, a molecule that exhibits mA chemisorption may be an ambidentate ligand that can provide 2, 4 or even 6 electrons to the surface bound state. An example is benzene. In transition metal chemistry, benzene is typically bound as an η^6 ligand and formally provides 6 electrons to the binding with the metal atom.[24] Such arene complexes often do not exhibit facile arene displacement by simple 2-electron donor molecules or ligands.[29] If facile displacement of an arene from a metal surface by carbon monoxide were observed, then it is unlikely that an η^6 surface binding is extant. An η^6-benzene ligand is, however, subject to displacement by a better arene donor such as mesitylene; on a surface, this type of potential displacement could be monitored by mass spectroscopy. In a few transition metal complexes, arenes are bound as η^4 or diene ligands, e.g. η^6-$(CH_3)_6C_6$-Ru-η^4-$C_6(CH_3)_6$. Such a four-electron donor molecule should be displaceable by another potential four-electron donor molecule, e.g. CH_3NC, and with some thermal activation, by a strong field, two-electron donor molecule. We generally may anticipate facile displacement of two-electron donors by stronger field two-electron donors or by multi-electron donors, of four-electron donors by stronger field four-electron donors or by six-electron donors, etc.

Finally, the case of molecules that undergo extensive rehybridization or rearrangement on chemisorption must be considered. For a rehybridized acetylene binding as in **1**, the acetylene ligand formally becomes a four-electron donor. In this case, displacement by a stronger field, four-electron donor molecule should be possible. There is evidence in cluster chemistry that CH_3NC, a potential four-electron donor, can displace an acetylene bound analogously to **1** from cluster-acetylene complexes.[30,31] Also a much stronger field, two-electron donor molecule might effect the displacement if sufficient thermal activation were provided.

A molecule that rearranges to a new molecule, e.g. propyne to allene or CH_3NC to CH_3CN would be subject to the same displacement consideration discussed above;and of course,displacement of a rearranged molecule would fully delineate an mAR process.[32] On the other hand, a molecule that rearranges on chemisorption to a bound molecular fragment should be relatively resistant to displacement by a molecule that exhibits molecular associative chemisorption. Thus, an acetylene that has rearranged on chemisorption to give, for example, a species analogous to **2** should not be displaceable by simple 2- or even 4-electron donor molecules. Acetylene and propyne should show the greatest tendency of the acetylenes to undergo this type of rearrangement because only one hydrogen atom migration is required. 2-Butyne unless it first rearranges to 1-butyne should be relatively resistant to a rearrangement to a chemisorbed fragment.

A special case of the formation of a molecular fragment by dissociative chemisorption, mDF, would be the direct generation of a CCH_2 fragment from ethylene and a benzyne C_6H_4 species from benzene. A cluster example of the latter is found in the reaction of benzene with trosmium carbonyl clusters in which the molecule $H_2Os_3(CO)_9C_6H_4$ is formed[33] and the C_6H_4 fragment is bound as shown schematically in **3**

3



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Mesitylene[34] or hexamethylbenzene is much less likely to exhibit this type of dissociative fragmentation. In principle, molecular fragments are displaceable by other molecules that exhibit dissociative chemisorption but a discussion of this special case of displacement reactions will not be pursued here.[35]

A final comment is in order regarding the non-uniformity of the chemisorbed state. More than one chemisorbed state may be present on a surface. For example, the heat of chemisorption of carbon monoxide falls as the surface coverage increases. This is a phenomenon observed in metal coordination chemistry; ligands are more tightly bound in a coordinately unsaturated complex than in a saturated complex. For molecularly chemisorbed CO, the primary effect of degree of surface coverage will be thermodynamic and not structural; in all instances, the CO should be bound only through the carbon atom. There could be structural variance in that some chemisorbed CO molecules could be oriented over one metal atom at the surface, some over the midpoint of a metal-metal vector and some over the center of three metal atoms. This latter variance should not qualitatively affect CO displacement reactions. In contrast, a molecule like acetylene might yield on some metal surfaces several structural states depending upon the degree of coverage. The initial states of chemisorption on a low Miller index face of a metal could yield primarily an mARF state. Then as the surface reactivity falls an mARH state could be favored. Finally at high coverages, a relatively weakly bound mA-η^2 state could be generated. Displacement reactions with two- and four-electron donor molecules could in principle delineate the types and concentrations of chemisorbed states. For high Miller index faces of a metal crystal or for polycrystalline metal, a distribution of chemisorbed states would be expected. Nevertheless, a quantitative study of displacement reactions could provide a characterization of chemisorbed states.

A systematic study of displacement reactions in combination with the modern-day surface science techniques of Auger, LEED, photoelectron and energy-loss spectroscopy[1] and flash pyrolysis experiments may provide fairly accurate structural characterizations of chemisorbed molecules. Displacement studies have greater applicability than flash desorption experiments simply because the latter may be complicated by the thermal reactivity of the chemisorbed species. Displacement reaction studies are really quite essential for polyatomic molecules chemisorbed on a surface because these studies can provide information about (1) the strength of the binding and the hierarchy of ligand field strengths with respect to metal surfaces for comparison with metal complexes and metal clusters,[17,23,31] (2) the possible rehybridization within the molecule on chemisorption and (3) rearrangement of the molecule in the chemisorption process. Table I summarizes the types of chemisorption processes and states with their chemical characteristics.

We are indebted to the Energy Research and Development Administration for support of this research.

E. L. Muetterties,[36,37*] J. C. Hemminger[38]
G. A. Somorjai*, Department of Chemistry
and Lawrence Berkeley Laboratory,
University of California,
Berkeley, California 94720

Table I. Chemisorption Processes and States

Class	Notation	Description	Example	Thermal Desorption Behavior	Displacement Reaction Behavior	Analog in Coordination Chemistry
1	mA_R	Molecular associative and thermally reversible.		Original molecule desorbed.		$Ni(PR_3)_3+PR_3 \rightleftharpoons Ni(PR_3)_4$
	$mA_R\text{-}\eta^1$	As above with one atom of the molecule bonded to the surface.	CO on Pt.	CO desorption.	Displaced by other 2-electron donor molecules.	$[CpMo(CO)_2]_2+2CO \rightleftharpoons [CpMo(CO)_3]_2$
	$mA_R\text{-}\eta^2$	As above with two atoms of the molecule bonded to the surface.	C_2H_4 on Cu.	C_2H_4 desorption.	Displaced by other 2-electron donor molecules.	$Ir(CO)ClL_2+C_2H_4 \rightleftharpoons Ir(CO)ClL_2(C_2H_4)$
2	mD_R	Molecular dissociative and thermally reversible (oxidative addition rx.).	H_2 on metals.	Original molecule desorbed.	Generally not displaced by donor molecules.	$Rh^{I}Cl(PR_3)_3+H_2 \rightleftharpoons Rh^{III}Cl(H)_2(PR_3)_3$
3	$mD_I\text{-}M_R$	Molecular dissociative and thermally irreversible with respect to reactant but clean surface regenerated (oxidative addition rx.).	HCN on Pt.	H_2, then $(CN)_2$ desorbed to leave "clean" metal surface.	Analogous to Class 2.	Will be rare in coordination chemistry.
4	mD_I	Molecular dissociative and thermally irreversible (oxidative addition rx.).	C_2H_4 on W.	H_2 desorbed in stages to leave carbon on the surface.	Not easily displaced.	$Ni^{0}(PR_3)_3+Br_2 \rightarrow Ni^{II}Br_2(PR_3)_3$
5.	mAP	Molecular associative with polymerization.	$(CN)_2$ on a metal.	Polymerization could be reversible or irreversible.	May be displaceable.	NiL_x+1,3-butadiene $\rightarrow xL$ + Ni(1,5,9-cyclododecatriene)

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Table I, cont'd.

6	mDP	Molecular dissociative with polymerization.	HCN on a metal.	H_2 desorption followed by a reversible depolymerization to $(CN)_2$ or an irreversible decomposition.	Not easily displaced.	Will be rare in coordination chemistry.
7	mARH	A molecular associative state derived from rehybridization of the molecule.	$RC\equiv CR$ on a metal.	Probably not reversible due to close proximity of R groups to the metal surface.	Probably not displaceable by a 2-electron donor molecule but displaced by a 4-electron donor.	$Co_2(CO)_8+RC\equiv CR\rightarrow 2CO+Co_2(CO)_6(\eta^2-\mu_2RC\equiv CR)$
8	mAR	A molecular associative state derived from rearrangement to a new molecule.	1,3-butadiene to give $CH_3C\equiv CCH_3$ on a metal.	New, bound molecule may be desorbable.	New molecule should be displaceable.	$Fe(CO)_5$+1,4-pentadiene$\rightarrow$2CO+$Fe(CO)_3$-(1,3-pentadiene)
9	mARF	A molecular associative state derived from rearrangement to a molecular fragment.	$CH_3C\equiv CH$ to give $C-C(CH_3)H$ on a metal.	Not reversible.	Not displaceable; fragment is not a good leaving group.	Will be rare in mononuclear coordination chemistry.
10	mDF	A molecular dissociative state derived from a molecular fragment.	$CH_3C\equiv CH$ to give CH_3CC on a metal.	Not reversible.	Fragment, not displaceable.	$D_2Os_3(CO)_{10}+C_2H_4\rightarrow D_2+CO+H_2Os_3(CO)_9CCH_2$

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3. C. B. Duke, Advan. Chem. Phys. 27, 1 (1974).

4. Positions for atoms chemisorbed on cubic close packed metal surfaces have been established for sodium, oxygen, sulfur, selenium and tellurium on Ni(100), sulfur on Ni(111), iodine on Ag(111), oxygen on W(110) and nitrogen on Mo(001). S. Andersson and J. B. Pendry, J. Phys. C 5, L41 (1972, J. E. Demuth, D. W. Jepsen and P. M. Marcus, Phys. Rev. Lett. 31, 540 (1973), 32, 1182 (1974). F. Forstmann, W. Berndt and P. Buttner, Phys. Rev. Lett. 30, 17 (1973), M. van Hove and S. Y. Tong, Phys. Rev. Lett. 35, 1092 (1975), and A. Ignatiev, F. Jona, D. W. Jepsen and P. M. Marcus, Surf. Sci. 49, 189 (1975).

5. The displacement reaction, a well-defined reaction in molecular coordination chemistry, comprises the displacement of a molecule, or an ion by another molecule or ion. For displacement reactions on surfaces, the term will be strictly limited to reactions in which a chemisorbed molecule is displaced as a molecule by a second molecule.

6. This article is limited to a discussion of chemisorption on metal surfaces but the concepts obviously can be extended to other types of surfaces.

7. In surface science, associative or dissociative refer explicitly to chemisorption processes of molecules that occur, respectively, with no fragmentation or with fragmentation of the molecule. In coordination chemistry, the term dissociative or associative reaction has a reaction mechanistic connotation. A dissociative reaction follows a step sequence

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of $ML_x \rightleftharpoons ML_{x-1}$ and $L' + ML_{x-1} \rightleftharpoons ML_{x-1}L'$, whereas associative follows the sequence $ML_x + L' \rightleftharpoons ML_xL'$ and $ML_xL' \rightleftharpoons ML_{x-1}L' + L$ (See C. H. Langford and H. B. Gray, "Ligand Substitution Reactions", Benjamin, New York, N. Y., Chap. 1). Since reactions of molecules with a metal surface will almost invariably be associative in a reaction mechanistic context, the less compact terminology of molecular associative and molecular dissociative chemisorption is recommended to avoid any confusion by scientists from different disciplines. New chemisorption terminology such as fragmented and intact, although more concise, might be less readily accepted by the surface science community because the present terms are of long-stadning usage.

8. K. Christmann and O. Schober, J. Chem. Phys. 60, 4719 (1974).

R. A. Sigehara and D. A. King, Surf. Sci. 58, 379 (1976).

9. J. C. Hemminger, E. L. Muetterties and G. A. Somorjai, to be published.

10. F. A. Cotton, J. Amer. Chem. Soc. 90, 6230 (1968), described a procedure for precisely defining certain structural features in the interaction of a metal atom with a ligand (a molecule, an atom or a group of atoms). The hapto notation (from the Greek haptein) denotes the connexity of the bonding, specifically, the number of atoms in the ligand that are within bonding distance of the metal atom; the short hand notation is η^x, where x denotes the connexity number. This explicit notational form is now widely used by inorganic and organometallic chemists. The connexity of the metal surface with respect to the molecule (ligand) can be designated by another convention used by coordination chemists, μ_x, where the subscript x denotes the number of metal atoms within bonding distance of the molecule (ligand). Thus, carbon monoxide bridge bonded to 2 or 3 metal atoms would be η^1-μ_2 and η^1-μ_3,

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respectively, and acetylene oriented (CC-axis) parallel to a metal surface and centered between 2 metal atoms would be η^2-μ_2.

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12. Cyanogen chemisorption studies have been described in brief form cf. F. P. Netzer, Surf. Sci. 52, 709 (1975) and 61, 343 (1976); M. E. Bridge, R. A. Marbrow and R. M. Lambert, Surf. Sci. 57, 415 (1976). CN derived from dissociative cyanogen chemisorption may be bound as (1) a CN^- ligand normal to the surface, (2) as a rehybridized three-electron ligand parallel to the surface or (3) as a polymer as suggested by Netzer or a triazine fragment, $(CN)_3$.

13. Madix and coworkers have elegantly used chemical information to define structural and mechanistic freatures of catalytic reactions; thermal desorption experiments have played a key role in their studies. See R. J. Madix and J. L. Falconer, Surf. Sci. 51, 546 (1975) and references therein.

14. V. W. Day, S. Abdul-Mequid, S. Dabestini, M. G. Thomas, W. R. Pretzer and E. L. Muetterties, J. Amer. Chem. Soc. 99, 743 (1977).

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17. E. L. Muetterties, Bull. Soc. Chim. Belg. 84, 959 (1975); Science 196, 839 (1977) and references therein.

18. M. G. Thomas, E. L. Muetterties, R. O. Day and V. W. Day, J. Amer. Chem. Soc. 98, 4645 (1976).

19. A. J. Deeming, S. Hasso, M. Underhill, A. J. Canty, B. F. G. Johnson, W. Jackson, J. Lewis and T. W. Matheson, J. Chem. Soc. Chem. Comm., 807 (1974); A. Deeming and M. Underhill, J. Chem. Soc. Chem. Comm. 277 (1973) and J. Organomet. Chem. 42, C60 (1972).

20. Displacement reactions on single crystal metal faces should be monitored by mass spectroscopic analysis of the gaseous species from the reaction and by Auger analysis before and after the displacement reaction with the latter normalized to an Auger spectrum of the metal surface after exposure of the reactant molecule to the clean metal surface. The initially chemisorbed molecule and the reactant molecules should contain different elements; exemplary pairs from this standpoint are CH_3CN-CO, C_2H_2-CH_3NC and C_2H_2-C_2N_2. For the mass spectral analysis of displaced molecules it is essential that chamber pumping speeds be high and that walls be as free as possible from the initially chemisorbed molecule to keep background at a minimum. The latter problem can be greatly minimized if after the first molecule is chemisorbed on the metal crystal face, an isolation cell is raised to shield the crystal and, unfortunately, the crystal backing and filament heating wires from the chamber. Then the chamber can be preconditioned with the reactant molecule before the displacement reaction is effected. The isolation cell is lowered, the crystal face is directed to the inlet of the mass spectrometer and then the reactant molecule is introduced. A multichannel analyzer should be used to plot crucial mass numbers during the exposure. In some cases it may be necessary to raise the metal crystal temperature above 300 K to obtain reasonable displacement rates; the upper temperature limit for these experiments is defined by the activation parameters of irreversible steps such as carbon formation.

21. An unambiguous characterization of the molecular displacement reaction requires a mass spectral identification of the displaced molecule.

22. Because the Auger experiment is typically a semi-quantitative analysis, proper choice of a displacing molecule with respect to its elemental composition and to the elemental composition of the chemisorbed molecule to be displaced is a crucial feature in the design of definitive experiments.

23. E. L. Muetterties, Bull. Soc. Chim. Belg. 85, 451 (1976).

24a. For general discussion of coordination complexes, their reactions and the mechanism of the reactions, see F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, 1972 (3rd edition), Chapters 19-26; J. C. Bailar, Jr., Ed. "The Chemistry of Coordination Compounds", Reinhold, New York, 1967; F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", John Wiley, New York, 1967 (2nd edition). (b) A synergistic bonding effect between two dissimilar chemisorbed molecules would obfuscate attempts to interpret a displacement reaction.

25. For a detailed discussion, see the review by J. A. Connor, "Topics in Current Chemistry: Metal Carbonyl Chemistry", F. L. Boschke, Ed., Springer Verlag, 1977.

26. Molecules like CO, acetylene and benzene which have low-lying π^* orbitals bind relatively strongly to metal atoms in coordination complexes provided that the metal atom is in a low oxidation state but either bind very weakly or not at all if the oxidation state is high. A similar behavior has been noted for molecules like CO and NO on metal surfaces; the binding is substantially reduced if the surface is partially oxidized, for example, with a halogen: cf. L. Lynds, Spectrochem. Acta, 20, 1369 (1964); C. R. Guerra and J. H. Schulman, Surf. Sci. 1, 229 (1967); M. Kobyashi and T. Shirasaki, J. Catal. 28, 289 (1973); R. A. Della Betta, J. Phys. Chem. 79, 2519 (1975); M. F. Brown and R. D. Gonzalez, J. Phys. Chem. 80, 1731 (1976); A. A. Davydov and A. T. Bell, to be published in J. Catal.

27. The chamber contamination problem for a molecule like iodine can be minimized with a crystal isolation cell.[20] At the low pressures employed in these displacement reactions, the thermodynamic probability of reaction between the chemisorbed molecule and reactants like I_2 or $(CN)_2$ typically will be low.

28. For example are R. C. Batezold, Adv. Catal. 25, 1 (1976) and J. C. Robertson and C. W. Wilmsen, J. Vac. Sci. Technol. 9, 901 (1972).

29. In $(\eta^6\text{-}C_6H_6)_2M$ molecules like $Cr(C_6H_6)_2$, one of the two arenes can be displaced by strong field, two-electron donor molecules like phosphines, but this displacement requires high temperatures and photochemical activation (M. G. Thomas, L. F. Stuhl and E. L. Muetterties, unpublished observations). Displacements of η^6-arene ligands from molecules like $C_6H_6ML_3$ have not been reported for two-electron donor molecules but are well established for six-electron, more basic arene molecules at elevated temperatures.

30. M. G. Thomas, W. R. Pretzer, B. F. Beier, F. J. Hirsekorn and E. L. Muetterties, J. Amer. Chem. Soc. 99, 743 (1977) and E. Band, W. R. Pretzer, M. C. Thomas and A. Kokorin, to be published.

31. We have initiated a study of displacement reactions with metal clusters to establish displacements series for two-electron donor ligands, four-electron donor ligands as typlified by acetylenes bound as in 1, etc.

32. To probe the possibility of rearrangement of a molecule on chemisorption to an isomer, i.e., a new molecule, it is important that the chemisorption behavior of isomers be examined. Thus, a chemisorption study of, for example, 2-butyne should be complemented with studies of the isomers 1-butyne, methylallene and 1,3-butadiene. If all four C_4H_6 isomers chemisorb without isomerization, their chemisorbed states will be differentiable (diffraction, spectroscopic and displacement reaction characteristics). Recently we have demonstrated that CH_3CN and CH_3NC chemisorb on Ni(111) without isomerization to CH_3NC and CH_3CN, respectively.[9] CH_3CN is the more thermodynamically stable isomer of the two.

33. A. J. Deeming and M. Underhill, J. Chem. Soc. Dalton Trans. 1415 (1974).

34. In fact, mesitylene behaves differently from benzene on the (111) and (110) faces of platinum (J. L. Gland and G. A. Somorjai, Surf. Sci. 41, 387 (1974); Adv. Colloid and Interface Sci. 5, 203 (1976)).

35. Structural definition of molecular fragments chemisorbed on a metal surface is far more difficult than for a molecular species. If hydrogen is present or is presumed to be present in the fragment as is the case for the important hydrocarbon fragments, a compositional characterization of the chemisorbed fragment cannot be accurately achieved. However, reactions of such chemisorbed fragments might yield desorbed reaction products that could provide a structural characterization. In some cases, it would be necessary to raise the pressure of the reaction system orders of magnitude above those for the typical displacement-type reaction to thermodynamically allow the desired reaction. For example, a CH_2 species now demonstrated in cluster chemistry (R. B. Calvert and J. R. Shapley, to be published) and probably preparable as a chemisorbed species from CH_2N_2 and a metal surface might react with cyanogen on a surface to give $CH_2(CN)_2$; a methyl fragment might react with cyanogen to give acetonitrile (a molecule weakly bound at a surface), and a benzyne with bromine to give o-$C_6H_4Br_2$ (surface bound benzyne probably will not generally flash desorb as benzyne because of the thermal reactivity of the remaining C-H hydrogen atoms).

36. Hitchcock Lecturer, University of California, Berkeley, 1977.

37. Present Address: Department of Chemistry, Cornell University, Ithaca, New York, 14853.

38. National Science Foundation Post-Doctoral Fellow, 1976-77.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720