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A Comparison between Ruthenium and Palladium with Regard to the Chemisorption of Carbon Monoxide on Metal Clusters Using Molecular Orbital Calculations

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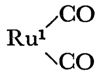
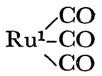
Self-consistent charge extended Hückel calculations for systems consisting of 1—3 CO molecules chemisorbed on 8-atom and 10-atom clusters of Ru and Pd are reported. The binding energies and overlap populations between Pd and C are always smaller than those between Ru and C. It was found that the multiple types of bondings between 2—3 CO and a surface metal atom were less stable for Pd than for Ru.

Ruthenium and palladium exhibit different properties in CO adsorption, though they are the same type of platinum metal.

It is firmly established for Pd that the ratio of CO molecules chemisorbed to the surface atoms (CO/M_s) is less than unity and that there are two types of bonding (linear and bridge) between CO and surface metal atoms.[1]

We showed recently, however, that the ratio of chemisorbed CO molecules to the total metal atoms of Ru-supported catalysts was more than unity; consequently, CO molecules form multiple bonds with the surface atoms in the following manner:[2,3]


(a)


(b)

Hereafter, the (a) and (b) types will be called "twin" and "trine" respectively, and Ru^1, "multivalent metal atom", for the sake of convenience.

Further support has been afforded to our proposal that the stoichiometry of CO/Ru_s is more than unity using hydrogen uptake measurements.[4,5] Taylor[4] and Dalla Betta[5] found that the atomic ratio of the hydrogen uptake to the surface Ru atoms (H/Ru_s) was almost 1. This stoichiometry was confirmed by an examination of the data reported by Kubicka[6] and the new data obtained in the present laboratory.

The uptake of H_2 and CO obtained by using the same $Ru-SiO_2$ catalysts as in previous papers[2,3] and the calculated CO/H (molecule/atom) are summarized in Table 1. The CO/H values of Ru catalysts supported on various other carriers; Al_2O_3 as given by Dalla Betta,[7] TiO_2 as given by Tauster *et al.*,[8] and active carbon *etc.*, as given by Vannice and Garten,[9] have values greater than 1. These data are also summarized in Table 1. This means that CO molecules more than 1 combine with a surface Ru atom.

The IR studies of chemisorbed CO on Ru show that two CO molecules form the twin-type coordination with a Ru atom which is positively charged.[10,11] Thus, the charge or electronic properties of surface metal atoms would be influenced by CO chemisorption of the twin or trine type.

Politzer and Kasten successfully explained the characteristic features of electronic-charge transfer in the systems of Ni_n–CO, where the n values ranged from 1 to 9, by using the self-consistent-charge (SCC) approximation in the extended Hückel method.[12] The present investigation has been undertaken with the purpose of elucidating the difference between Pd and Ru catalysts in these CO-chemisorbed states in relation to the electronic charge transfer by means of the SCC extended Hückel approximation.

Procedure

Model Clusters. The crystal lattice of Pd metal is face-center-cubic (fcc), while that of Ru metal is hexagonal close-packed (hcp). The calculations have been performed for 10-atom clusters, as is shown in

Table 1. Hydrogen and CO adsorption on various Ru catalysts

Catalysts	t/°C	H_2[ml(stp)/g]	t/°C	CO[ml(stp)/g]	CO/H	Ref.
0.367(mg-atoms/g) $Ru-SiO_2$-35-1	100	1.52	−78	9.93	3.27	
			150	11.28	3.71	
0.186 2	100	1.10	−78	6.77	3.08	
0.093 3	100	0.60	−78	4.57	3.81	
0.047 4	100	0.40	−78	2.55	3.19	
		H_2(μmol/g)		CO(μmol/g)		
5% $Ru-Al_2O_3$	21	82.7	21	373	2.3	7
0.5% $Ru-Al_2O_3$	21	15.1	21	116	3.8	7
0.23% $Ru-Al_2O_3$	21	9.3	21	57.3	3.1	7
2% Ru/TiO_2	r.t.	3.0	r.t.	7.2	1.2	9
5% Ru/Al_2O_3	r.t.	17.4	r.t.	35	1.01	9
4% Ru/C	r.t.	38	r.t.	160	2.11	9
2% $Ru-TiO_2$(reduction temp 200 °C)	25	H/M=0.23	25	CO/M=0.64	2.78	8
(reduction temp 500 °C)	25	H/M=0.06	25	CO/M=0.11	1.83	8

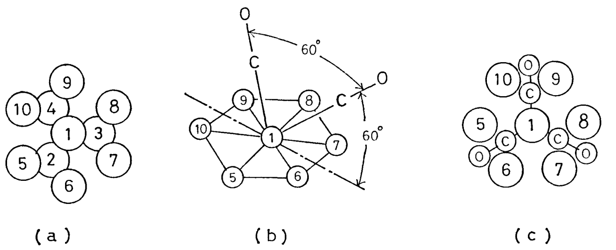


Fig. 1. Models for 10-atom cluster (a), M_{10}–$(CO)_2$ (b), and M_{10}–$(CO)_3$ (c).

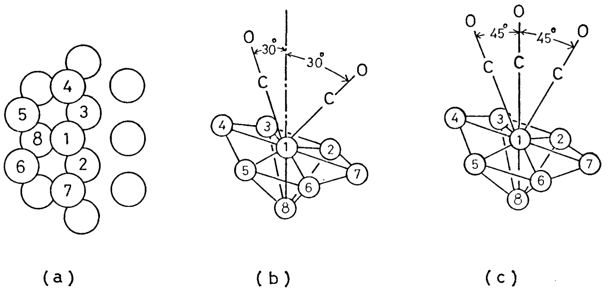


Fig. 2. Models for 8-atom cluster (a), M_8–$(CO)_2$ (b), and M_8–$(CO)_3$ (c).

Fig. 1(a). The atoms numbered 1 and 5—10 constitute the surface of Pd(111) or Ru(001). The atoms numbered 2, 3, and 4 correspond to the second layer.

It is presumed that the metal particles which are highly dispersed have the step sites, as is shown in Fig. 2(a). The model of the 8-atom cluster was also adopted. The atoms numbered 1, 4, and 7 constitute the edge of a stepped Pd(111) or Ru(001) surface. The 2, 3, and 8 atoms are second-layer with respect to the 1 and 4—7 atoms.

All the CO molecules bond to a central atom (numbered 1 in Figs. 1 and 2) through carbon atoms. In the present paper, models of the CO chemisorbed clusters are expressed, such as M_{10}–CO and M_8–$(CO)_2$. M is meant by Pd or Ru. The subscripts 10 and 8 indicate the clusters of Figs. 1 and 2 respectively. The subscripts of CO show the numbers of CO molecules adsorbed on the atom 1.

In M_{10}–CO, the C and O atoms are taken on the C_3-axis of C_{3v} symmetry. In M_{10}–$(CO)_2$ of Fig. 1 (b), two pairs of C and O are taken on the σ_h-plane of C_s symmetry, with the C–M–C angle of 60°. In M_{10}–$(CO)_3$ of Fig. 1(c), three pairs of C and O are taken on each of the three σ_v-planes of C_{3v} symmetry. Three C and atom 1 form a regular tetrahedral arrangement.

In M_8–CO, the atoms numbered 8, C, and O are taken on the C_2-axis of the C_{2v} symmetry. In M_8–$(CO)_2$ of Fig. 2 (b), the 1, 4, 7, and 8 atoms and two pairs of C and O are taken on one of the two σ_v-planes of the C_{2v} symmetry, with the C–M–C angle of 60°. In M_8–$(CO)_3$ of Fig. 2 (c), one of three CO is taken on the C_2-axis of the C_{2v} symmetry, with the C–M–C angle of 45°.

All the nearest-neighbor distances between metal atoms are taken as metallic values of 2.65 Å and 2.75 Å for Ru and Pd respectively. The Ru–C bond length is taken as 2.00 Å, which is close to that of 1.92 Å in $Ru_3(CO)_{12}$.[13] The two kinds of Pd–C bond length are taken as 2.00 Å for the sake of comparison with Ru, and as 2.25 Å; this brought about a desirable density of states in comparison with the UPS spectra. Palladium carbonyl complexes to be referred to for the Pd–C bond length are lacking. The C–O bond length is taken as 1.15 Å, which is identical with Politzer and Kasten's report[12] and close to the 1.128 Å of free CO.

Calculation. Computation was carried out by using the SCC extended Hückel method. Each molecular orbital, Ψ_i, is written as a linear combination of the occupied valence orbitals of various atoms:

$$\Psi_i = \sum_{jk} C_{ijk}\phi_{jk},$$

where ϕ_{jk} is an atomic orbital j on the atom k.

The diagonal elements of the Hamiltonian matrix, H_{ii}, are given in terms of the valence-state ionization energy according to the procedure of Basch, Viste, and Gray:[14]

$$-H_{ii} = A + BQ,$$

where Q is the charge on the atom. Basch *et al.*[14] applied A and B as functions of the average electron configuration as well as the atomic orbitals, but in the present paper A and B were adopted as functions of the atomic orbitals only, because of the difficult convergence and because of the insufficient spectroscopic data on Ru and Pd.[15] The A and B determined by spectroscopic data[15] as well as other input data are listed in Table 2.

The overlap elements, S_{ij}, were culculated by using Slater orbitals. The interactions among all the nearest-neighbor atoms are taken into account. The orbital exponents (ζ) obtained by Clementi *et al.*[16,17] were adopted except for 5s and 5p. The ζ_{5p} of Ru or Pd is lacking in Clementi's table,[17] but ζ_{5p} was postulated to be equal to ζ_{5s} according to Slater's rule. The ζ_{5s} and ζ_{5p} of Pd or Ru were determined as the minimum values so as not to give rise to negative eigenvalues of the determinant S_{ij}, since negative ones were produced when Clementi's ζ_{5s} was adopted. The ζ_{5s} and ζ_{5p} of Ru are accidentally coincident to those of Pd in two significant figures.

The off-diagonal elements of the Hamiltonian matrix were approximated by using Cusachs formula:[18]

$$H_{ij} = (1/2)S_{ij}(2 - |S_{ij}|)(H_{ii} + H_{jj})$$

The calculation generally went through 5—35 iterations, giving a Mulliken charge distribution varying by less than 0.01 on each atom between successive cycles. As did Rein, Fukuda, Win, and Clark, we used the damping parameter in the iteration process to avoid divergence or oscillation;[19] convergence was forced by changing this damping parameter.

The density of states (DOS) was calculated from the converged coefficients, C_{ijk}, in every occupied level and multiplied by the Gaussian function, with a standard deviation of 2.0 eV. In the present paper, energy levels are expressed in values relative to the highest occupied molecular orbital (HOMO), which is taken as zero or the Fermi level (E_f). Fassaert and van der Avoird's paper[20] was referred to.

Table 2. Parameters of the calculation

Orbital exponents	Ru	Pd		C	O
4d	3.2032	3.4044	2s	1.6083	2.2458
5s, 5p	2.6	2.6	2p	1.5679	2.2266

	Ru		Pd			C		O	
(eV)	A	B	A	B		A	B	A	B
4d	10.78	4.36	12.43	11.54	2s	16.60	19.48	32.37	16.78
5s	7.36	8.05	8.33	7.99	2p	11.26	6.49	15.84	17.36
5p	5.91	5.36	3.70	7.06					
								A[a)]	B[a)]
					2s			32.37	13.28
					2p			15.84	13.44

a) In negative charge of Q.

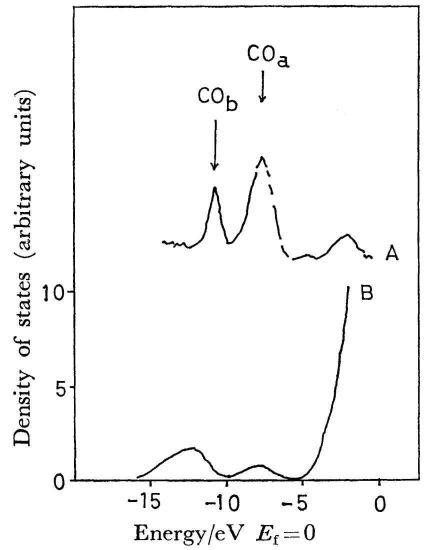


Fig. 3. Comparison between density of states for Ru_{10}–CO and UPS spectra of CO-covered Ru(001) surface. (A): UPS (He_{II}) spectra of Ru(001) covered 15 Langmuir CO, (B): density of states calculated for Ru_{10}–CO.

There were great differences in the total energies (ground states) of various models. It should be noted that the convergent states in the SCC approximation are not necessarily minimum in energy. The total energies will not be discussed in the present paper.

Results and Discussion

Density of States (DOS). The DOS values for Ru_{10}–CO are shown in Fig. 3, along with the UPS spectra of CO adsorbed Ru(001).[21)] The DOS of the Ru_{10} cluster almost overlaps with that of Ru_{10}–CO over −5 eV and almost equals zero under −5 eV, so the DOS line is omitted in Fig. 3. The results of calculation agree with the UPS spectra on the CO$_a$ band (−7.6 eV).

The DOS for Pd_{10}–CO (Pd–C=2.25 Å) and the Pd_{10} cluster are shown in Fig. 4, along with the UPS spectra of CO-adsorbed Pd(111).[22)] In the case of Pd–C=2.00 Å, the higher band (−7 or −6 eV) in the DOS of CO is very small; hence, the figure is omitted. The results of calculation agree with the UPS spectra on the CO$_b$ band (−11.2 eV). The higher band (CO$_a$) in the DOS of CO (B in Fig. 4) agrees with the 5σ level obtained by Chen *et al.* in the SCF-XαSW calculation for Pd_5–CO.[23)]

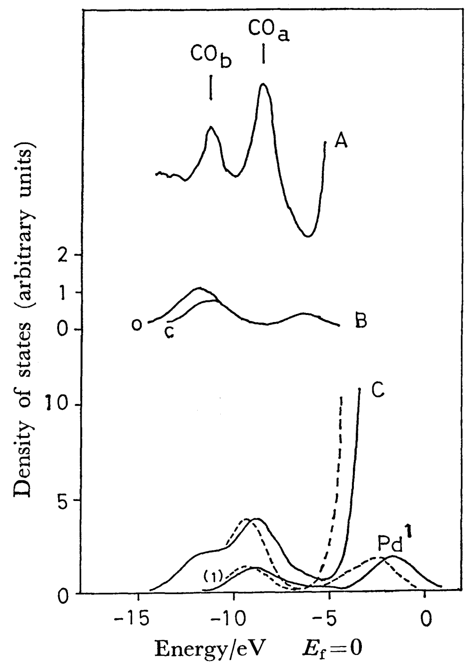


Fig. 4. Comparison between density of states for Pd_{10}–CO and UPS spectra of CO adsorbed Pd(111). (A): UPS (He_{II}) spectra of Pd(111) exposed to 2×10^{-7} Torr of CO, (B): density of states for C and O calculated in Pd_{10}–CO; (C): density of states for the whole and for central Pd^1 in Pd_{10}–CO (——) and Pd_{10} (----).

The DOS of the Ru_{10} cluster scarcely differs from that of Ru_{10}–CO, but the DOS of the Pd_{10} cluster (C in Fig. 4) has two important characteristcs. First, the DOS of the Pd_{10} cluster is widespread over a range lower than that of Ru_{10} and changes to a higher range upon adsorbing CO. Secondly, about half of the DOS of Pd^1 exists in a range lower than −5 eV, and this DOS is not influenced by the presence of CO. These two characteristcs suggest that electrons of Pd_{10} are more stable and that fewer electrons take part in bonding with CO compared with Ru_{10}. This difference will be discussed numerically in the next section.

Population Analysis. Mulliken's atomic gross population (AGP), the atomic net population (ANP), the atomic bond population (ABP), and the atomic orbital-bond population (AOBP) were analyzed by using the converged C_{ijk} values. All the ANP properly have values less than the numbers of the valence electron on the atom. All the ABP of all the models except for Pd_{10}–$(CO)_3$ are positive, but negative ABP of Pd–Pd were contained in the Pd_{10}–$(CO)_3$; consequently, it can be presumed that such a state of chemisorption as in this model is not possible.

In the 10-atom cluster, M_{10}–$(CO)_2$ has C_s symmetry, unlike the other models. In the 8-atom cluster, M_8–$(CO)_3$ contains two different pairs of C and O atoms. Consequently, a detailed comparison among the same metal and the same cluster was omitted.

In AGP, the 10-atom cluster and 8-atom cluster systems are summarized in Tables 3 and 4 respectively. All the AGP of C (AGP-C) in the adsorbed CO are greater than the 3.695 of free CO. In Ru, all the AGP-C are greater than 4 (valence electrons of C). These results indicate the presence of an overall transfer of electrons from Ru to C, a so-called "back donation." In Pd_{10}–CO, the AGP-C of Pd–C=2.25 Å is greater than 4 and that of Pd–C=2.00 Å. This corresponds to the result of DOS presented above; that is, in Pd–C=2.00 Å, the higher band in DOS of CO is very small. The AGP-C values of Pd_{10}–$(CO)_2$, Pd_8–$(CO)_2$, and Pd_8–$(CO)_3$ are smaller than in all other models. The back donation can be taken as a measure of the strength of the bond between metal and carbon, so that the strength of the bond between a multivalent Pd and two or three C may be weak.

In the 8-atom cluster, all the AGP of oxygen have values greater than 6; that is, oxygen atoms have negative charges. This agrees with the general tendency found by another investigation.[12] In the 10-atom cluster, these AGP values of oxygen are less than 6. This suggests that the 8-atom cluster gives more suitable results of calculation.

In the AGP of a central atom, Ru^1 or Pd^1, without CO, those of the 8-atom cluster are greater than those of the 10-atom cluster, and they (8-atom cluster) are greater than the number of each valence electron (Ru: 8, Pd: 10). The transfer of electrons from the nearest-neighbor atoms to a central atom occurs and facilitates the back donation. Consequently, the step site (8-atom cluster) forms stronger bonds between metal and C, and also forms twin or trine easily. The values AGP—8.00 of Ru^1 are always greater than the values

TABLE 3. THE ATOMIC GROSS POPULATION OF C, O, AND CENTRAL METAL ATOM IN THE 10-ATOM CLUSTERS

	CO[a)]	M_{10}[b)]	M_{10}–CO	M_{10}–$(CO)_2$[c)]	M_{10}–$(CO)_3$
Ru^1 [d)]	—	7.900	7.972	8.507	7.931
C	3.695	—	4.040	4.137	4.224
O	6.305	—	5.689	6.433	5.632
Pd-C=2.00 Å					
Pd^1 [d)]	—	9.227	9.389	9.923	—
C	3.695	—	3.867	3.758	—
O	6.305	—	5.514	6.294	—
Pd-C=2.25 Å					
Pd^1 [d)]	—	9.227	9.491	9.945	—
C	3.695	—	4.123	3.743	—
O	6.305	—	5.747	6.294	—

a) Free CO. b) Metal cluster. c) AGP of C or O are the average values of two different atoms in C_s symmetry. d) Central atom numbered 1 in Fig. 1.

TABLE 4. THE ATOMIC GROSS POPULATION OF C, O, AND CENTRAL METAL ATOM IN THE 8-ATOM CLUSTERS

	CO[a)]	M_8[b)]	M_8–CO	M_8–$(CO)_2$	M_8–$(CO)_3$[c)]
Ru^1 [d)]	—	8.107	8.310	8.401	8.493
C	3.695	—	4.238	4.143	4.079
O	6.305	—	6.470	6.441	6.421
Pd-C=2.00 Å					
Pd^1 [d)]	—	10.005	9.971	9.925	9.938
C	3.695	—	3.962	3.722	3.741
O	6.305	—	6.350	6.322	6.300
Pd-C=2.25 Å					
Pd^1 [d)]	—	10.005	9.962	9.997	9.958
C	3.695	—	3.924	3.687	3.726
O	6.305	—	6.357	6.312	6.294

a) Free CO. b) Metal cluster. c) AGP of C or O are the averages of two different atoms which are located in the center and at the side. d) Central atom numbered 1 in Fig. 2.

AGP—10.00 of Pd[1] in all models. This indicates that the Ru–C bonding is more stable than that of Pd–C.

The binding energy (E_b) between the central metal atom and C, and the C–O stretching frequencies (ν) in various models are summarized in Table 5. The ν of C–O were evaluated by fitting the equation given by Baerends and Ros[24] to the ABP of CO. Except for M_{10}–CO and Ru_8–CO, the calculated ν values are close to the experimental values (1900—2200 cm^{-1}), so the SCC approximation seems reasonable. The discrepancies in the ν values of M_{10}–CO and Ru_8–CO are ascribed to Baerends's equation,[24] which was derived from carbonyl complexes. These complexes contain 4—6 CO, and neither Pd nor Ru was dealt with as a transition metal atom in the Baerends's paper.[24]

The binding energy, E_b is the E_{ab} value proposed by Pople *et al.*[25] These $|E_b|$ values decrease with an increase in the number of CO; that is, the bonding of twin or trine is weaker than linear bonding. The E_b values of Pd–C=2.00 Å properly have greater negative values than those of Pd–C=2.25 Å because of their shorter bond lengths. The E_b values of Ru–C always have greater negative values than the E_b values of Pd–C, and the E_b values of Pd–C=2.25 Å, which gives a result closer to the UPS spectra, are particularly small negative values, less than half those of Ru–C. On the whole, it is clear that the bonding of Pd–C, especially the bonding of twin or trine, is more unstable than that of Ru–C.

The ABP between the central metal atom and C in various models are summarized in Table 6, while the ABP between C and oxygen in various models are summarized in Table 7. The total ABP of Ru–C have greater values than those of Pd–C in each model. Contrary to the case of metal-C, the total ABP of CO in Ru are always smaller than those in Pd. The total ABP of CO in each model are always smaller than those of free CO. This shows that the overall increase in electron density between metal and C causes a decrease in the electron density between C and oxygen; this tendency agrees with the well-known description of transition-metal complexes involving car-

TABLE 5. C–O STRETCHING FREQUENCIES AND BINDING ENERGIES IN 8-ATOM AND 10-ATOM CLUSTERS

	M_{10}-CO	M_{10}-(CO)$_2$[a]	M_{10}-(CO)$_3$	M_8-CO	M_8-(CO)$_2$	M_8-(CO)$_3$[b]
Ru-C=2.00 Å ν/cm^{-1}	1234	1923		1852	1915	1982
Pd-C=2.00 Å ν/cm^{-1}	1611	2219		2062	2217	2233
Pd-C=2.25 Å ν/cm^{-1}	1620	2240		2096	2256	2253
Ru-C=2.00 Å E_b/eV	−1.94	−1.57	−1.44	−2.68	−1.80	−1.52
Pd-C=2.00 Å E_b/eV	−1.73	−1.32		−2.14	−1.25	−1.06
Pd-C=2.25 Å E_b/eV	−0.83	−0.67		−1.02	−0.67	−0.61

a) The averages of two different atoms in C_s symmetry. b) The averages of the central and side atoms.

TABLE 6. ATOMIC BOND POPULATION BETWEEN THE 1 ATOM AND CARBON ATOMS IN VARIOUS CLUSTERS

		M_{10}-CO	M_{10}-(CO)$_2$[a]	M_{10}-(CO)$_3$	M_8-CO	M_8-(CO$_2$)$_2$	M_8-(CO)$_3$[b]
Ru-C=2.00 Å	σ	0.478	0.348	0.304	0.405	0.352	0.285
	π	0.161	0.181	0.125	0.231	0.183	0.160
	Total	0.639	0.528	0.429	0.635	0.535	0.445
Pd-C=2.00 Å	σ	0.429	0.208		0.274	0.208	0.184
	π	0.078	0.075		0.113	0.074	0.066
	Total	0.507	0.283		0.388	0.282	0.250
Pd-C=2.25 Å	σ	0.320	0.150		0.179	0.152	0.136
	π	0.026	0.038		0.055	0.034	0.034
	Total	0.347	0.187		0.234	0.186	0.170

a) The averages of two different atoms in C_s Symmetry. b) The averages of the central and side atoms.

TABLE 7. ATOMIC BOND POPULATION BETWEEN C AND O

		CO[a]	M_{10}-CO	M_{10}-(CO)$_2$[b]	M_{10}-(CO)$_3$	M_8-CO	M_8-(CO)$_2$	M_8-(CO)$_3$[c]
Ru-C=2.00 Å	σ	0.614	0.478	0.602	0.448	0.600	0.600	0.600
	π	0.715	0.048	0.468	−0.124	0.423	0.463	0.506
	Total	1.329	0.526	1.070	0.324	1.023	1.063	1.105
Pd-C=2.00 Å	σ	0.614	0.463	0.613	—	0.647	0.600	0.605
	π	0.715	0.292	0.656	—	0.549	0.657	0.666
	Total	1.329	0.755	1.268	—	1.196	1.256	1.271
Pd-C=2.25 Å	σ	0.614	0.431	0.626	—	0.652	0.605	0.621
	π	0.715	0.304	0.667	—	0.570	0.681	0.676
	Total	1.329	0.734	1.293	—	1.222	1.285	1.297

a) Free CO. b) The averages of two different atoms in C_s symmetry. c) The averages of the central and side atoms.

Table 8. Atomic orbital bond population between the 1 atom and C in various clusters

		M_{10}-CO	M_{10}-CO)$_2$[a]	M_{10}-(CO)$_3$	M_8-CO	M_8-(CO)$_2$	M_8-(CO)$_3$[b]
Ru-C=2.00 Å	4d	0.040	0.227	0.060	0.233	0.187	0.153
	5s	0.201	0.160	0.149	0.194	0.163	0.136
	5p	0.398	0.140	0.220	0.209	0.185	0.156
Pd-C=2.00 Å	4d	0.012	0.055		0.101	0.063	0.063
	5s	0.175	0.239		0.225	0.195	0.163
	5p	0.320	0.021		0.062	0.024	0.024
Pd-C=2.25 Å	4d	−0.004	0.027		0.042	0.023	0.026
	5s	0.090	0.124		0.139	0.130	0.111
	5p	0.261	0.037		0.054	0.033	0.033

a) The averages of two different atoms in C_s symmetry. b) The averages of the central and side atoms.

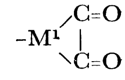
bonyl groups. In the 8-atom cluster, the total ABP of CO and ν increase, while those of metal-C decrease, with the number of CO. This tendency agrees with the view reported by Davydov and Bell[11] concerning the band shift of the IR spectra.

The ABP of π-orbitals in Pd–C are less than half those of Ru–C in every model. Since the ABP of π-orbitals result from the back donation of electrons from metals, the greater values of the ABP of π-orbitals as well as the total ABP in Ru–C show that Ru adsorbs CO more strongly than Pd.

The steep falls of the ABP (π-orbitals) in Pd_8–(CO)$_2$ and Pd_8–(CO)$_3$ and of the total ABP in Pd_{10}–(CO)$_2$ seem to explain why no experimental data of twin or trine types of CO chemisorption in Pd exist.

The AOBP between the 1 atom and C in various models are summarized in Table 8. In the AOBP of metal-C, remarkable differences between Pd and Ru are observed. The AOBP of the 4d-orbital in Ru–C are always more than double those in Pd–C. It seems an important factor for the stabilization of the bonding, especially, the bonding of twin or trine, that 4d-orbitals take part in the bond formation between metal and carbon. In Pd–C, the AOBP of 5s or 5p are greater than those of 4d. In the calculation of Chen *et al.*[23] for Pd_5–CO by the SCF-XαSW method, the ratio of the charge density in s, p, and d orbitals is 1:1:2. In the present calculations, the result for Pd_8–CO is close to that for Pd_5–CO obtained by Chen *et al.*[23] The great charge density of the d-orbital obtained by Chen *et al.*[23] arises from their taking the four Pd atoms as nearest neighbors. In the three hypothetical models Pd_8–(CO)$_2$, Pd_8–(CO)$_3$, and Pd_{10}–(CO)$_2$, the AOBP of 4d-orbitals are very small compared with Pd_8–CO. This is why twin or trine do not exist in CO-adsorbed Pd metal. The small AOBP of the 4d-orbital in Pd_{10}–CO have not yet been solved.

C–C Interaction. In the calculations described above, the overlap elements among carbon atoms were not taken into account. Further calculations were performed by placing the overlaps between carbon atoms in the matrix elements according to the following scheme of M_8–(CO)$_2$ and M_{10}–(CO)$_2$:



The various atomic populations of 10-atom and 8-atom clusters are summarized in Tables 9 and 10 respectively. The M^1–C bond length is taken as the same 2.00 Å in both Ru and Pd metals. The C–C bond length also results in a value of 2.00 Å when the M_8–(CO)$_2$ and M_{10}–(CO)$_2$ are used as models.

Table 9. The atomic population[a] of M_{10}-(CO)$_2$ with a C-C bond

Metal	AGP		Total ABP		AOBP (M^1-C)	
Ru	Ru^1	8.424	Ru-C	0.440	4d	0.181
	C	4.250	C-O	0.952	5s	0.092
	O	6.482	C-C	0.487	5p	0.166
Pd	Pd^1	9.945	Pd-C	0.228	4d	0.080
	C	4.132	C-O	1.010	5s	0.116
	O	6.368	C-C	0.541	5p	0.033

a) The values of carbon and oxygen are averages of two different atom in C_s symmetry.

Table 10. The atomic population of M_8-(CO)$_2$ with a C-C bond

Metal	AGP		Total ABP		AOBP (M^1-C)	
Ru	Ru^1	8.313	Ru-C	0.442	4d	0.184
	C	4.266	C-O	0.953	5s	0.097
	O	6.478	C-C	0.499	5p	0.160
Pd	Pd^1	9.904	Pd-C	0.232	4d	0.086
	C	4.089	C-O	1.014	5s	0.121
	O	6.356	C-C	0.561	5p	0.024

In all the evidence, the case taking the C–C overlap shows the same tendency as the preceding case taking no C–C overlap. The same discussion as in the preceding sections therefore holds.

The ABP of the C–C bond of the Pd cluster are greater than those of Ru contrary to the ABP of M^1–C. This is coincident with the tendency of the C–O bond.

The binding energies, E_b, values of M^1–C (E_{M-C}), of C–O (E_{C-O}), and of C–C (E_{C-C}) are summarized in Table 11. The $|E_{C-O}|$ and $|E_{C-C}|$ values of Ru are smaller than those of Pd. This tendency is comparable to that of ABP.

Concluding Remarks

Generally speaking, the experimental results show that no CO chemisorption of the twin or trine type is found on Pd, but is found on Ru metal.

Table 11. The binding energy of carbon atom in 8-atom and 10-atom clusters with a C–C bond

Cluster		E_{C-M}/eV	E_{C-O}/eV	E_{C-C}/eV
10-atom	Ru	−1.28	−8.87	−1.11
	Pd	−1.07	−10.58	−1.47
8-atom	Ru	−0.94	−8.86	−1.41
	Pd	−0.55	−10.42	−1.85

Calculations for the model Pd_{10}–$(CO)_3$ cluster gave negative ABP among the Pd atoms, suggesting that there is no trine type CO adsorption on the 10-atom Pd cluster.

From a comparison of Ru with Pd concerning twin-type adsorption on the 8-atom and 10-atom clusters, stability differences in bonding between two CO molecules and these metals were deduced, as is shown by the following inequality relationships:

1. AGP of $Ru^1 > 8$ (valence electron numbers of Ru)
   AGP of $Pd^1 < 10$ (valence electron numbers of Pd)
   This shows that an over-all donation to Ru^1 occurs more easily than to Pd^1.
2. AGP of C in Ru>4
   AGP of C in Pd<4
   This shows that an over-all back donation from Ru metal occurs more easily than from Pd metal.
3. (Total ABP of Ru–C)>(total ABP of Pd–C)
4. (AOBP of 4d in Ru–C)≫(AOBP of 4d in Pd–C)
5. ($|E_b|$ of Ru–C)>($|E_b|$ of Pd–C)

All five of these relationships indicate that the twin-type CO adsorption on 8-atom and 10-atom Ru clusters are more stable than those on Pd. Thus, the calculated results account well for the experimental observations.

References

1) R. P. Eischens and W. A. Plinskin, *Adv. Catal.*, **10**, 1 (1958); R. P. Eischens, S. A. Francis, and W. A. Plinskin, *J. Phys. Chem.*, **60**, 194 (1956); *J. Chem. Phys.*, **22**, 1786 (1954).

2) M. Kobayashi and T. Shirasaki, *J. Catal.*, **28**, 289 (1973).

3) M. Kobayashi and T. Shirasaki, *J. Catal.*, **32**, 254 (1974).

4) K. C. Taylor, *J. Catal.*, **38**, 299 (1975).

5) R. A. Dalla Betta, *J. Catal.*, **34**, 57 (1974).

6) H. Kubicka, *J. Catal.*, **12**, 223 (1968).

7) R. A. Dalla Betta, *J. Phys. Chem.*, **79**, 2519 (1975).

8) S. J. Tauster, S. C. Fung, and R. L. Garten, *J. Am. Chem. Soc.*, **100**, 170 (1978).

9) M. A. Vannice and R. L. Garten, *J. Catal.*, **63**, 255 (1980).

10) M. F. Brown and R. D. Gonzalez, *J. Phys. Chem.*, **80**, 1731 (1976).

11) A. A. Davydov and A. T. Bell, *J. Catal.*, **49**, 332 (1977).

12) P. Politzer and S. D. Kasten, *J. Phys. Chem.*, **80**, 385 (1976).

13) R. Mason and A. I. M. Rae, *J. Chem. Soc., A*, **1968**, 778.

14) H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, **44**, 10 (1966).

15) C. E. Moore, "Atomic Energy Levels," Natl. Bur. Stand. (U. S.), (1949), Vol. 1; (1958), Vol. 3.

16) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

17) E. Clementi, D. L. Raimondi, and W. P. Reinhardt, *J. Chem. Phys.*, **47**, 1300 (1967).

18) L. C. Cusachs, *J. Chem. Phys.*, **43**, s157 (1965).

19) R. Rein, N. Fukuda, H. Win, and G. A. Clarke, *J. Chem. Phys.*, **45**, 4743 (1966).

20) D. J. M. Fassaert and A. van der Avoird, *Surface Sci.*, **55**, 291 (1976).

21) D. Menzel, *J. Vac. Sci. Technol.*, **12**, 313 (1975).

22) D. R. Lloyd, C. M. Quinn, and N. V. Richardson, *Solid State Commun.*, **20**, 409 (1976).

23) B.-H. Chen, D. C. Foyt, and J. M. White, *Surface Sci.*, **67**, 218 (1977).

24) E. J. Baerends and P. Ros, *Mol. Phys.*, **30**, 1735 (1975).

25) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).