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Relative Stabilities of Hydridocarbonyl and Formyl Complexes of Rh and Pd: A Theoretical Study

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The energy variations accompanying the migration of the hydrogen atom of the hydridocarbonyl complexes H*M*CO (*M* = Rh, Pd), leading to the formation of the formyl species *M*CHO, have been theoretically studied by means of effective core potential SCF and configuration interaction calculations. The process studied involves the formation of an activated complex and the height of the corresponding energy barrier is found to be markedly different for the two considered metal atoms. In particular, in the case of the Pd complex the presence of a positive charge substantially lowers the energy barrier and favors the formation of the formyl derivative. On the other hand, the energetics concerning the Rh complex are not appreciably influenced by the presence of a positive charge. The difference in behavior of the two metal atoms is rationalized on the basis of the analysis of the electron distribution. The present results indicate that the apparent difficulty of the insertion process cannot be attributed to the different stabilities of the hydridocarbonyl and metalloformyl complexes.

INTRODUCTION

Reactions of syngas (CO/H_2) offer an excellent opportunity to study fundamental problems of catalysis, such as the selectivity of catalysts and the role of promoters and supports. For example, by a proper choice of a support or promoter, palladium can be made to catalyze formation of either methane or methanol (*1*). This and similar examples are well known but not fully understood. It can be expected that a theoretical study on certain mechanistic aspects could be helpful in this respect. Moreover, the results of such a study are of interest to organometallic chemistry in general.

Metalloformyl complexes have been proposed as intermediates in the catalytic hydrogenation of carbon monoxide (*2, 4*). The insertion of CO into the metal–H bond (actually, migration of H atom) is not a generally accepted mechanism mainly because it has never been clearly confirmed by experimental evidences. In particular, the isolation of formyl-coordinated species under normal conditions is difficult due to the easy dissociation and elimination of CO and formation of hydride complexes (*2, 5*). However, the analogous insertion reaction of CO into a metal–alkyl bond producing a stable acyl complex (*5*) is a well-characterized process. The difference in behavior in CO insertion bonds has been ascribed to the difference in bond strengths (*M*–H 200–250 kJ mol^{-1}, *M*–CH_3 80–120 kJ mol^{-1} (*6, 7*)). The syntheses of metalloformyl complexes of Os, Rh, Ir, and Re have been reported (*7–11*). It has been suggested that positive oxidation states of the metal center can contribute to the stabilization of these complexes (*8*). Spectroscopic studies of CH_3OH adsorbed on nickel have given some evidence for the existence of formyl species (*12*). Moreover, in order to explain the enhanced activity of Pd catalysts in CH_3OH synthesis when Pd^+ ions are present, the hypothesis that Pd^+ ions stabilize the formyl intermediate and lower the

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energy barrier for the insertion reaction of CO into the Pd–H bond could be suggested (*13–15*). Recently reported results (*16*) of ab initio minimal basis set calculations on closed-shell H_2PdCO and $[HPdCO]^+$ systems support this view since the computed activation energy for the insertion process was found to be much smaller for the positively charged system.

The present work reports results of effective core potential (ECP), Hartree–Fock, and configuration interaction calculations on neutral and cationic HRhCO and HPdCO systems. The aims of the present investigation were (i) to compare the behavior of different metals in zero-oxidation state, such as Pd, which is characterized by a d^{10} (^1S) atomic ground state, and Rh which on the contrary has a d^8s^1 (^4F) electronic configuration in the gas phase, and (ii) to investigate the possible influence of higher formal oxidation states of the metal atoms on the energetics of the insertion of CO into a metal–H bond.

Despite the considerable limitation represented by the use of a single ligand-free metal atom to model the active center in the insertion reaction it is hoped that this study can provide some useful information on the feasibility of this particular mechanism.

METHOD

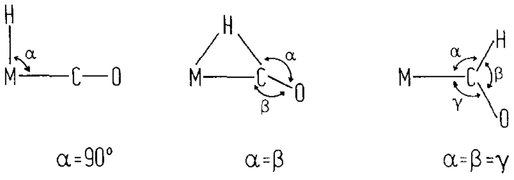
Computational Aspects

The effective core potential operator (*17*) describing the effect of the 36 core electrons of Rh and Pd and the 2 core electrons of C and O has been taken from Refs. (*18–20*), respectively. The basis set consisting of [4*s*, 2*p*, 5*d*] primitive Gaussian functions for Rh and Pd (*21*) and of [4*s*, 4*p*] for C and O (*22*) has been contracted to double-zeta, [2*s*, 1*p*, 2*d*] and [2*s*, 2*p*], respectively. A [4*s*1*p*/2*s*1*p*] basis has been adopted for the hydrogen atom (*23*).

The ground state wavefunction determined according to the spin and symmetry restricted Hartree–Fock method is improved by means of a configuration interaction (CI) calculation. Singly and doubly excited configurations generated from the reference SCF determinant (SD CI) are treated according to the configuration selection procedure and energy extrapolation criterion of Buenker and Peyerimhoff (*24, 25*). The dimensions of the variational CI space range from 2000 to 3000, depending on the particular geometry and spin state of the considered system.

RESULTS

The reaction path for the process H–*M*–CO → *M*–CHO has been investigated at three representative points, assuming some constraints on the values of the valence angles in order to reduce the number of variable internal coordinates (Chart 1). At first glance the imposition of some constraints appears rather arbitrary. Actually, the assumption is corroborated by the fact that more careful geometry optimizations of the transition state in similar complexes (*26–29*) clearly indicate that the migration reactions occur through the formation of a three-center transition state with H or CH_3 groups bridging the metal–CO bond. All the three considered structures are assumed to be planar lying in the *xy* plane and will be referred to hereafter as H*M*CO (I), *M*HCO (II), and *M*CHO (III). The *M*–H, *M*–C, C–O, and C–H bond lengths have been consecutively optimized at CI level in this order. Therefore, the optimum geometry search has been only partially carried out. However, in other test calculations not reported here, it was found that the most important energy variations are those associated with the changes in bond lengths explicitly considered. In the case of neutral



I II III

CHART 1

TABLE 1

Equilibrium Bond Lengths and Population Analysis for HMCO and $[HMCO]^+$ Species

System structure	HRhCO			$[HRhCO]^+$			HPdCO			$[HPdCO]^+$		
	I	II	III	I	II	III	I	II	III	I	II	III
$R_{M\text{-H}}$ Å	1.51	1.61	—	1.51	1.59	—	1.66	>2.30	—	1.48	1.55	—
$R_{M\text{-C}}$ Å	1.92	1.84	1.95	2.03	2.07	1.89	2.32	2.20	2.08	2.37	2.26	2.00
$R_{\text{C-O}}$ Å	1.15	1.15	1.21	1.13	1.15	1.19	1.15	1.17	1.22	1.13	1.15	1.18
$R_{\text{C-H}}$ Å	—	—	1.12	—	—	1.10	—	—	1.12	—	—	1.10
Population												
Pd 5s	0.44	0.26	0.12	0.23	0.12	0.06	0.40	0.13	0.30	0.17	0.10	0.06
5p	0.08	0.08	0.04	0.04	0.03	0.01	0.19	0.10	0.05	0.06	0.06	0.03
$4d_{x^2-y^2}$	1.30	1.92	0.68	0.99	1.07	1.20	1.42	1.92	1.56	1.27	1.90	1.45
$4d_{z^2}$	1.43	1.26	1.98	1.11	1.61	1.00	1.94	1.97	1.89	1.86	1.94	1.85
$4d_{xy}$	1.90	1.64	1.98	1.97	1.55	1.99	1.97	1.94	1.99	1.99	1.53	1.99
$4d_{yz}$	1.86	1.83	1.95	1.97	1.96	1.96	1.98	1.94	1.97	2.00	1.98	1.98
$4d_{xz}$	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
$4d_{\text{tot}}$	8.49	8.64	8.60	8.04	8.21	8.15	9.31	9.77	9.42	9.11	9.34	9.25
Charge	−0.01	+0.02	+0.24	+0.69	+0.64	+0.78	+0.10	0.00	+0.23	+0.66	+0.50	+0.66
C 2s, 2p	3.68	3.68	3.80	3.71	3.71	3.70	3.72	3.71	3.90	3.78	3.76	3.70
O 2s, 2p	6.26	6.27	6.44	6.09	6.07	6.24	6.20	6.25	6.34	6.09	6.05	6.19
H 1s, 2p	1.05	1.08	1.00	0.90	0.86	0.82	1.18	1.03	0.98	0.79	0.69	0.78

HMCO complexes the linear form is more stable than the form I by 20.0 and 29.3 kJ mol^{-1} for M = Rh and M = Pd, respectively. The M–H, M–C, and C–O distances in the collinear arrangement have been computed equal to 1.68, 2.13, and 1.15 Å for M = Rh and 1.60, 2.34, and 1.15 Å for M = Pd, respectively.

Despite the fact that the linear form of HMCO has been found to be more stable than the structure I, the choice of the latter as starting point of the model reaction path is justified considering that in mononuclear complexes of transition metal atoms (typically the d^8 planar complexes) the insertion of a coordinated CO group into the M–R bond always occurs when CO and R are in *cis* position. Moreover, structure I can be considered as representative of the situation occurring on a metal surface (assuming a one-center mechanism) whereas the collinear arrangement can exist only on some special sites (edges, corners). The results of the geometry optimizations carried out for structure I are reported in Table 1 for neutral and cationic complexes of Rh and Pd.

The character and the electron distribution maps (EDM) concerning some selected "in plane" MOs of a' symmetry are illustrated in Figs. 1–4 (the EDM of the Rh^+ complex are not shown, their shape being very similar to that of the corresponding neutral Rh structures). In structure I the 6a' MO is the most important MO in determining the strength of the M–H bond (Fig. 1);

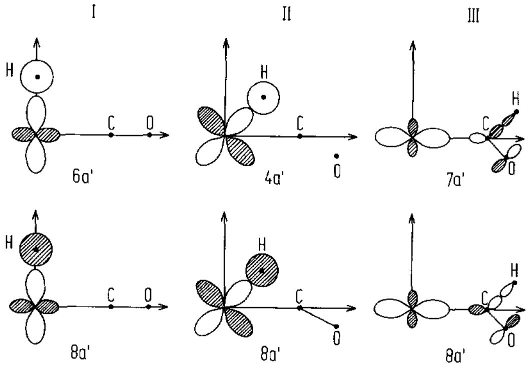


FIG. 1. Character of some selected bonding and antibonding MOs in HMCO systems. The molecule lies in the xy plane. The 6a', 4a', and 7a' are doubly occupied MOs which substantially contribute to the stability of structures I, II, and III, respectively (see Chart 1). The 8a' MO is the lowest unoccupied MO in $[HRhCO]^+$, HRhCO, and $[HPdCO]^+$ and is the highest singly occupied in HPdCO.

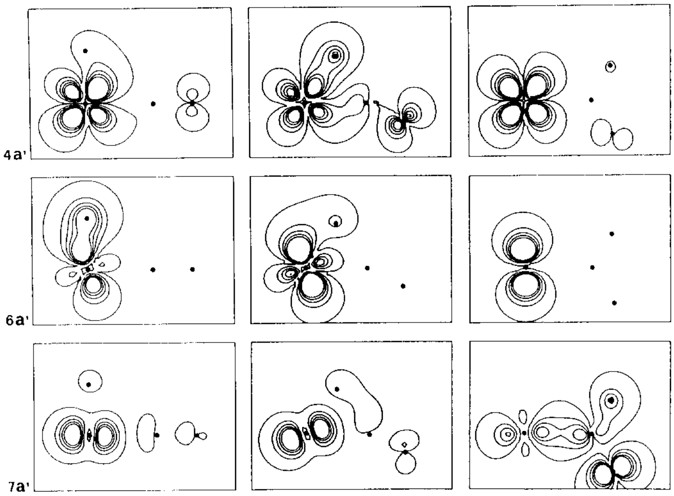


FIG. 2. Electron density contour maps for selected *MO*s of HRhCO (from left to right structures I, II, and III; see also Chart 1). The contour lines are separated by 0.03 electrons/a.u.^{3}.

the $4a'$ *MO* in structure II is a combination of the d_{xy} orbital of the metal atom with the $1s$ H orbital and is responsible for the bonding of H in the bridge position (Fig. 1); finally, in structure III the formyl group is bound to the metal atom mainly through the $7a'$ *MO* (Fig. 1). The $8a'$ *MO*, on the other hand, has antibonding character in all three structures considered. This latter *MO* is the singly occupied HOMO of HPdCO and the LUMO of Pd^+, Rh, and Rh^+ complexes. As a consequence, the ionization from the $8a'$ *MO* increases the strength of the Pd–H bond and causes a contraction of the Pd–H distance (from 1.66 to 1.48 Å; see Table 1). On the other hand, the ionization of HRhCO does not remove electronic charge from the Rh–H region and does not significantly affect this bond distance (1.51 Å).

A feature common to both Rh and Pd complexes is that the ionization of the metal atom produces an electronic state ca-

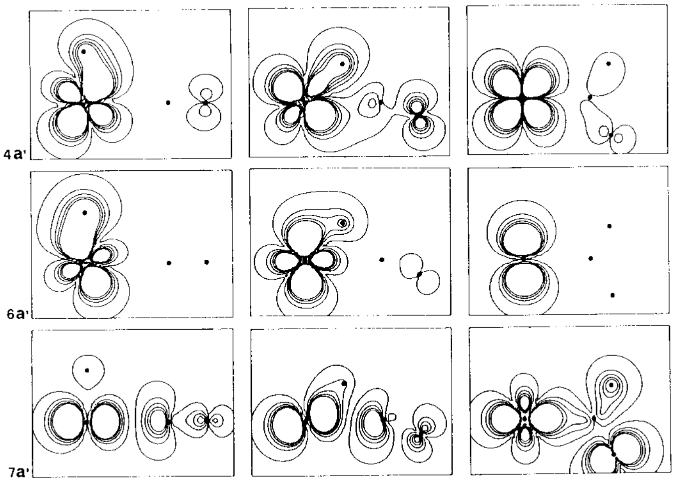


FIG. 3. Electron density contour maps for selected *MO*s of $[HPdCO]^+$. See Fig. 2 for definitions.

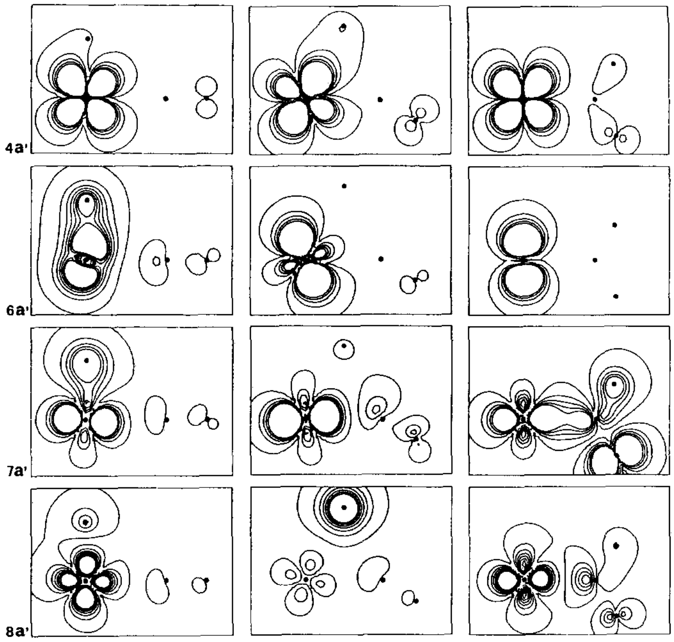


FIG. 4. Electron density contour maps for selected *M*Os of HPdCO. See Fig. 2 for definitions.

pable of minor π-back-bonding. This explains the fact that the *M*–C distances are larger in the cationic forms (weaker *M*–C bond) and that the C–O distances are shorter than those of the neutral forms and very similar to that of the free CO molecule (1.13 Å).

In $[HMCO]^+$ complexes the net charge on the metal centers is found to be equal to 0.69 and 0.66 for Rh and Pd, respectively, and this suggests that the metal atoms are in a formal oxidation state +1.

According to the present model of the reaction path the structure II should correspond to a transition state which, in the case of neutral and positively charged Rh complexes, can be reached against an energy barrier of 68.1 and 75.6 kJ mol^{-1}, respectively (Table 2 and Fig. 5). The Pd complexes considered in structure II present a very interesting feature: the energy of the cationic form is 48.5 kJ mol^{-1} higher than that of the corresponding structure I but is stable toward dissociation, while the neutral form is unstable with respect to the dissociation in PdCO ($E = -51.1412$ a.u.) + H ($E = -0.4997$ a.u.) (see also Table 2). The origin of the instability of the PdHCO (II) complex must be attributed

TABLE 2

Total Energies (a.u.) and Energy Differences (kJ mol^{-1}) for H*M*CO and $[HMCO]^+$ Systems at SCF and SD CI Levels

		Structure (see Chart 1)		
		I	II	III
HRhCO	E_{SCF} (a.u.)	−44.1774	−44.1445	−44.1867
	ΔE_{SCF} (kJ mol^{-1})	0.0	86.1	24.5
	E_{CI} (a.u.)	−44.4905	−44.4605	−44.4847
	ΔE_{CI} (kJ mol^{-1})	0.0	68.1	15.0
$\|HRhCO\|^+$	E_{SCF}	−43.9648	−43.9315	−43.9542
	ΔE_{SCF}	0.0	87.4	51.0
	E_{CI}	−44.2655	−44.2366	−44.2565
	ΔE_{CI}	0.0	75.6	23.4
HPdCO	E_{SCF}	−51.3812	−51.3544	−51.3845
	ΔE_{SCF}	0.0	67.3	−8.36
	E_{CI}	−51.6705	−51.6340	−51.6805
	ΔE_{CI}	0.0	95.7	26.3
$\|HPdCO\|^+$	E_{SCF}	−51.1282	−51.1033	−51.1226
	ΔE_{SCF}	0.0	65.2	14.6
	E_{CI}	−51.4298	−51.4113	−51.4327
	ΔE_{CI}	0.0	48.5	− 7.5

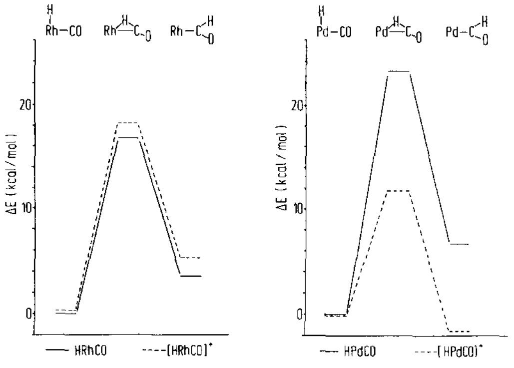


FIG. 5. Relative SD CI energies of the structures I, II, and III with respect to structure I in HRhCO, HPdCO, and respective cations (see also Table 2) (1 kcal mol^{-1} = 4.18 kJ mol^{-1}).

to the electronic situation which is peculiar to this species. As mentioned above, the 8*a*′ *M*O which in structure II mainly involves the d_{xy} orbital on the metal center and the orbital centered on the hydrogen atom has antibonding character even more pronounced than that in the case of structure I. The occupancy of the 8*a*′ *M*O reduces the bonding effect due to the 4*a*′ *M*O (Fig. 1).

The importance of this effect, which can occur only for the neutral Pd complex, may be understood from the analysis of the EDM of Fig. 4. The electron density associated with the open-shell 8*a*′ *M*O is almost completely localized around the hydrogen nucleus even for a relatively short Pd–H distance (2.30 Å). At the same time, no other *M*O of symmetry *a*′ has an appreciable amplitude in the Pd–H region (Fig. 4), and this favors the dissociation of the Pd–H bond. The situation is further clarified if one compares the EDMs of Fig. 4 with those of Figs. 2 and 3, where an important accumulation of electronic charge in the *M*–H internuclear region of *M*HCO (II) is clearly evident.

Another effect accompanying the hydrogen migration into the bridge position of the neutral Pd complex is the destabilization of all doubly occupied *M*Os in structure II with respect to structures I and III. This can be attributed to the increase in Coulombic repulsion occurring when hydrogen occupies the bridge position. In fact, as shown in our previous work (*21*), the region of the σ-bonding of Pd–CO is characterized by a decrease in electron density with respect to the separated fragments as a consequence of the repulsion between the 5σ *M*O of CO and the d_σ electrons of Pd. The importance of this kind of repulsion on the insertion mechanism is indirectly demonstrated by the different population of the d_{xy} orbital in PdHCO (II) with respect to the other Rh and Pd structures. In particular, in the unstable PdHCO (II) form, the d_{xy} orbital is occupied by two electrons while in the other cases the population of this orbital is about 1.5 electrons (Table 1).

The final *M*CHO structure (III) is the only one for which a direct comparison of the optimized geometrical parameters with experimental data is possible. In fact, a rare example of Rh formyl complex characterized in solid state by X-ray crystallography has been reported (*8*). The experimental Rh–C, C–O, and C–H distances, 1.896, 1.175, and 1.09 Å, respectively, compare well with our computed values for the $[RhCHO]^+$ species, 1.89, 1.19, and 1.10 Å, respectively (Table 1). The Rh–CHO fragment was found to be planar with Rh–C–O and Rh–C–H angles of 130°.

The *M*CHO (III) formyl complexes are 16–25 kJ mol^{-1} less stable than the hydridocarbonyl structures for M = Rh, Rh^+, and Pd and about 4 kJ mol^{-1} more stable in the Pd^+ complex (Table 2). In structure III the 7*a*′ *M*O (Fig. 1) plays a crucial role in bonding the metal center to the formyl group. This orbital is always doubly occupied in the systems considered, so producing a net metal–carbon bond. However, in the neutral PdCHO (III) complex the single occupancy of the 8*a*′ *M*O which presents a nodal plane in the *M*–C region (Fig. 4) causes a lengthening of the *M*–C bond with respect to the ionic molecule and slightly destabilizes the structure. This effect is quite small since the electron density of the 8*a*′ *M*O is mainly concentrated on the Pd atom (0.71

electrons). Similarly, the unpaired spin density in the $[RhCHO]^+$ (III) complex is localized on the metal center.

The structure of the CHO fragment is similar in the four systems considered and a general effect observed is the charge shift toward the oxygen atom which leaves the metal atoms partially positive even in the neutral complexes.

The insertion reaction of CO into the *M*–H bond has recently been studied by other theoretical groups. Anikin *et al.* (*16*) reported minimal basis set all-electron calculations on closed-shell H_2PdCO and $[HPdCO]^+$ systems. It was found that for the H_2PdCO complex the energy barrier to H migration is about 250 kJ mol^{-1} and the formyl complex is 188 kJ mol^{-1} less stable than the hydridocarbonyl one, while no barrier and a greater stability of the final form are observed for the $[HPdCO]^+$ compound. The stabilization of the intermediate $[PdHCO]^+$ (II) complex was attributed to the ability of this structure to "discard" the excess population of the 5*s* Pd orbital, needed to form a hydride bond, on the 4*d* orbitals. These results were qualitatively reproduced by the current computational scheme used, provided that the same geometry as that in Ref. (*16*) was assumed. Correlation effects, which in principle could be responsible for the observed discrepancy between our results and those of Anikin *et al.* (*16*), do not change the qualitative behavior found at the Hartree–Fock level. The high energy barrier and the low stability of the formyl species in H_2PdCO are essentially due to the fact that in Ref. (*16*) the geometries of the initial, intermediate, and final structures were not optimized. In particular, the chosen Pd–CO distance is too short with respect to our optimized value (2.0 Å as against about 2.37 Å). This destabilizes the hydridocarbonyl (I) and the formyl (III) molecules more than the activated complex (II) and would explain the zero energy barrier found by Anikin *et al.* (*16*).

Two recent papers (*26, 27*) addressed the problem of the insertion of H into the Mn–CO and $[Pd–CO]^+$ bonds with ab initio SCF and CI calculations. At the Hartree–Fock level the hydridocarbonyl (I) and the formyl (III) HMnCO complexes have comparable stabilities and are separated by an energy barrier of about 46 kJ mol^{-1}. The inclusion of correlation effects through SD CI calculations increases the barrier and strongly destabilizes the formyl complex (*26*). The difference between SCF and CI results has been attributed to the unbalanced description of Mn–CO and Mn–CHO bonds in SCF (*26*). The $[HPdCO]^+$ system was considered only in the initial (I) and final (III) forms without geometry optimization in order to check the effect of correlation on the energies of the two geometries (*27*). With respect to the SCF results, it was found that the introduction of correlation strongly stabilizes the formyl with respect to the hydridocarbonyl form (*27*). We found that, with respect to the initial hydridocarbonyl Rh and Pd structures (I), the height of the energy barrier is reduced in Rh, Rh^+, and Pd^+ when correlation effects are considered, while in PdHCO, which is virtually an unstable system, the correlation correction is much smaller and the barrier in CI is larger than that in SCF (Table 2). Moreover, the formyl structure (III) is destabilized by correlation effects by about 30–40 kJ mol^{-1} in the neutral form and stabilized by 20–25 kJ mol^{-1} in the charged systems with respect to the hydridocarbonyl complex.

In conclusion, a substantial difference was found in the behavior of Rh or Pd species and the HMnCO system since, according to the CI energies, the Mn formyl complex is unstable and spontaneously transforms into the original hydridocarbonyl compound (*26*). Further work is necessary in order to clarify whether this difference reflects a real situation or is due to methodological difficulties.

DISCUSSION AND CONCLUSIONS

In this work we have considered the mechanism of H migration from a metal center to a coordinated CO molecule and its possible relevance to some aspects of heterogeneous catalysis. The use of a single metal atom to model the reaction can be considered very primitive and rather arbitrary. Nevertheless, the interest for this simple model originates from the experimental observation that for several metals the active catalysts in methanol synthesis have ions (chemically extractable and detectable) in the steady state of the working catalysts. A correlation between activity and ion concentration has been established (*14*, *15*). This seems to indicate that one (or more) molecular intermediate of the CH_3OH synthesis is more easily formed or stabilized on ions; for instance, formyl and formate have been proposed as potential candidates (*2*, *4*). If the rate-determining step of the reaction involves the formation of molecular M–CHO or M^+–CHO species, then quantum-chemical calculations can contribute to elucidate the electronic mechanism governing this interaction.

The calculations reported here are based on the hypothesis that the formation of formyl species starting from hydridocarbonyl complexes occurs through an activated complex where the H atom bridges the M–C bond.

The height of the energy barrier and the reaction mechanism strongly depend on the electronic structure and oxidation state of the metal center. In particular, for M = Rh, Rh^+, Pd^+, the energy barrier is about 50–75 kJ mol^{-1} and the migration reaction is of intramolecular type, while for M = Pd the barrier is higher than the energy required to dissociate the Pd–H bond and the reaction is of intermolecular type. In other words, it appears that the first step in the formation of the formyl complex starting from the hydridocarbonyl complex in neutral HPdCO is the detachment of the H ligand followed by the attack of the highly reactive H atom on the electrophilic carbon atom. According to this mechanism the H atom does not necessarily belong to the Pd coordination sphere and can be provided by the medium where the reaction occurs ("spillover" hydrogen).

The significant difference among the activated complexes RhHCO, $[RhHCO]^+$, $[PdHCO]^+$, and PdHCO is that in the latter complex the HOMO is a singly occupied *MO* with net antibonding character between Pd and H. The occupancy of this *MO* strongly destabilizes the intermediate complex resulting in the dissociation of the molecule into Pd–CO + H. The removal of one electron from this *MO* produces three effects: the resulting positive charge is mainly localized on the Pd atom which can be considered in a formal oxidation state +1, the height of the barrier is significantly reduced, and the final formyl complex is stabilized.

With respect to the reaction of the neutral Pd system, the Pd^+ ion favors the migration process and stabilizes the final product. This result qualitatively agrees with the experimental observation that active Pd catalysts in methanol synthesis show a clear sympathetic correlation between the catalytic activity and the concentration of the Pd^+ ions on one side (i.e., the activity increases with the ion concentration) (*14*) and a correlation with the concentration of the formyl group on the other side (*4*).

On the other hand, we found a very similar behavior between Rh and Rh^+ species. In fact in this case the ionization process involves mainly the Rh atom and does not influence the strength of the Rh–H bond.

An important result common to all the considered systems is that the Rh and Pd formyl complexes are not particularly unfavored with respect to the hydridocarbonyl species. The small energy differences found between the two structures seem to indicate a comparable stability of the two forms (Table 2). Therefore, according to the results of the present calculations, the factor inhibiting the migration reaction is not the tendency of metalformyl Rh or Pd species to transform into hydridocarbonyl complexes but must be identified with the difficult formation of the reaction intermediate. The stretching of the relatively strong M–H bond occurring when H moves toward the CO molecule is an energy-demanding process which is not compensated by the creation of a new three-center M–H–C bond. In the M–C axial region in fact, corresponding to the σ-bonding of M–CO, there is a decrease in electron density due to the Coulombic repulsion originated by the interaction of the diffuse 5σ lone pair of CO with the d_σ orbitals of Rh or Pd (*21*). In the transition state where H bridges the M–C bond both nuclear and electron repulsions are increased and the bond is weakened.

Turning back to the problem mentioned in the first paragraph of the Introduction, the following can be concluded at this stage. Reactions like methanol synthesis can indeed be promoted by the presence of Pd^{n+} species and that opens the possibility to speculate that one of the promoter (or support) effects could be that to stabilize Pd^{n+} in a reducing environment. Results of this paper indicate that this aspect of the promoter function is less important with Rh than with Pd.

These conclusions are valid for an isolated neutral or ionic metal atom. The possible effect of other substituents (metal atoms or ligands) has not been considered explicitly here. Other ab initio calculations (*30, 31*), however, have shown that the formation of a small Pd cluster of Pd atoms does not remarkably change the atomic configuration which remains close to d^{10}; the d orbitals split to give a filled d band but also in a cluster of four Pd atoms the s band is empty (*30, 31*). It is still unclear whether this result must be attributed to the limitations of the theoretical method employed (in particular to the absence of the relativistic effects) or if more bonds are necessary in order to compensate the $d^{10} \rightarrow d^9s^1$ promotion energy required to form the metal–metal bonds and to allow the cluster to approach a more bulk-like situation. Therefore, significant changes in the qualitative behavior are not expected when a single Pd atom is replaced by a small Pd cluster. Possible collective effects of the massive metal are as yet unexplored.

On the contrary, it has been shown that on addition of two water molecules to a d^{10} Pd atom the d population goes down slightly to 9.8 and the ground state configuration increases its d^9s^1 character (*32*). A similar effect has been observed with other ligands (e.g., CO) (*21*). An extreme case is represented by the H ligand which changes dramatically the electronic configuration of the Pd atom from d^{10} to $d^{9.4}s^{0.4}$ (*33*). A Pd atom in such an electronic situation is expected to bind more strongly a second H atom than the CO ligand in the hypothetical $H_2Pd(d^9s^1)CO$ system. In this case a higher barrier to migration is expected to occur in the neutral form, and the SCF calculations of Anikin *et al.* (*16*) support this view. Dedieu *et al.* (*26, 27*) have considered the H migration reaction in $HMn(CO)_5$ and HMnCO systems but they found qualitatively similar reaction paths. The theoretical study of the alkyl migration in the complex $Pd(CH_3)(H)(CO)(PH_3)$ indicates that the reaction is endothermic by about 37 kJ mol^{-1} (*28*), a value close to that found here for the HPdCO system (26 kJ mol^{-1}).

On the basis of this meager evidence it seems that the factor determining the different reactivities of HPdCO and $[HPdCO]^+$ molecules is really the presence of the positive charge, and that, in general, ligands able to stabilize the Pd(I) oxidation state should favor the hydrogen migration reaction.

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