significantly alter the structural parameters for the heavy atoms.

In the electron diffraction investigation of the structure of trimethylphosphine sulfide, two different models were utilized, i.e., partially rotated methyl groups and methyl groups freely rotating. The model with the methyl groups rotated by 42.7 ± 7.3° appeared to give a better fit to the diffraction pattern. The substitution of all three hydrogens on one of the methyl groups by deuterium does not provide data for checking the partially rotated model. A model with tilted methyl groups was not tried in the electron diffraction investigation, but is is expected that it would provide as good a fit to the diffraction curves as the partially rotated model. There have been many cases where "tilted" methyl groups have been found[14] but little evidence for partially rotated methyl groups.

Results obtained from measurements of the infrared spectra of solid $(CH_3)_3PS$ and $(CD_3)_3PS$ at low temperature contradict some of the assignments made by Rojhantalab et al.[4] from the study of the Raman spectra alone. Changes have been presented for the assignments of the CH_3 rocks, the PC_3 skeletal modes, and possibly the SPC_3 rocking modes. For $(CH_3)_3PS$ and the isotopic species, the fundamental frequencies of the carbon-hydrogen stretching and bending motions fall within the same range as those observed[16-19] for the corresponding modes in $(CH_3)_3P$. This indicates that the force constants for methyl stretching and bending motions are not affected by bonding to the sulfur atom. On the other hand, the frequencies for the PC_3 skeletal motions are significantly altered. The force constant for the PC_3 stretch increases from 2.78 mdyn/Å in the free base to 3.38 mdyn/Å in the sulfur adduct. This increase in the magnitude of the PC_3 stretching force constant is consistent with the shortening of the P-C bond length from 1.846 Å in $(CH_3)_3P$[16] to 1.814 Å in $(CH_3)_3PS$. The CPC bond angle increases from 98.9° in the free base[16] to 104.41° in the sulfur adduct. In all previous studies on the adducts of trimethylphosphine,[8-10,12] similar changes in the geometry of $(CH_3)_3P$ upon adduct formation has been accompanied by an increase in the magnitude of the PC_3 stretching force constant. These observations have been explained by the VSEPR model.

The potential energy distributions (Tables V-VII) for the observed bands show an abundance of mixing among the fundamental modes of vibrations. For instance, the P=S and PC_3 stretching motions couple extensively and a very large degree of mode mixing is also observed between the CD_3 rocking and PC_3 stretching motions. Each of the five interaction constants, F_β', F_β'', $F_{\epsilon\beta}$, $F_{\epsilon\beta}'$ and $F_{\epsilon\beta}''$ (table VIII), affect the relative energies of the methyl rocking motions. While the mechanisms behind the interactions are not obvious in all cases, the interaction F_β' may be interpreted as a measure of the repulsive force between the equatorial hydrogen atoms of the three different methyl groups of the molecule.

The fact that the three observed infrared bands in the spectral range for lattice modes have shift factors and frequencies very similar to those of Raman lines observed in the spectrum of the corresponding molecule suggests that the Raman lines are probably due to librational modes. There is also evidence that the infrared bands may be doublets, which would indicate that the tentative determined space groups is not correct. Far-infrared spectral studies of an oriented single crystal would provide additional information on the crystal symmetry.

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Registry No. $(CH_3)_3PS$, 2404-55-9; $(CH_3)_2(CD_3)PS$, 117800-84-7; $(CH_3)(CD_3)_2PS$, 117800-85-8; $(CD_3)PS$, 71889-34-4; $(CH_3)_3P^{34}S$, 117800-86-9; D, 7782-39-0; ^{34}S, 13965-97-4.

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CO_2 Interaction with $HCr(CO)_5^-$: Theoretical Study of the Thermodynamic Aspects

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Ab initio LCAO-MO-SCF calculations have been carried out for the acid-base adduct involved in the insertion reaction of CO_2 into the metal-hydrogen bond of $HCr(CO)_5^-$. This adduct, the geometry of which has been determined, is found to be more stable than the reactants. Its further evolution toward the formate product and the role of an ancillary ligand dissociation are discussed in terms of molecular orbital interactions.

There is much current interest in carbon dioxide coordination and reactivity. The insertion reaction of CO_2 into the metal-hydride bond of hydrido transition-metal complexes (reaction 1)

$$CO_2 + L_nMH \rightarrow L_nM(OCHO) \qquad (1)$$

is observed in several instances[1,2] and has been one of the most thoroughly investigated reactions, especially from the point of view of its mechanism, owing to its apparent simplicity and its prototype character. Experimental studies using the $HM(CO)_5^-$ hydrido carbonyl complexes (M = Cr, Mo, W) as substrates[3-6] have shown that, at variance with the insertion into a metal-alkyl bond,[7,8] the insertion into the metal-hydride bond probably involves the dissociation of an ancillary carbonyl ligand. This dissociation might be triggered by a preassociation of the hydrido complex with CO_2.[4] Support for this hypothesis was gained from the

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(2) For more recent examples, see: (a) Fong, L. K.; Fox, J. R.; Cooper, N. J. *Organometallics* **1987**, *6*, 223. (b) Kundel, P.; Berke, H. *J. Organomet. Chem.* **1986**, *314*, C31. (c) Sullivan, B. P.; Meyer, T. J. *Organometallics* **1986**, *5*, 1500.

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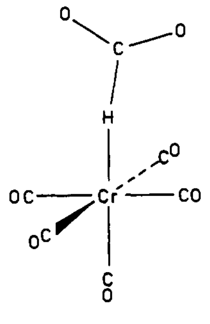
observation, in the reaction of BH_3 with $HCr(CO)_5^-$, of a transient IR band attributed to a similar acid–base adduct.[5] Yet unequivocal experimental evidence for the occurrence of such an acid–base adduct in the CO_2 insertion reaction is lacking. A theoretical investigation of reaction 1 might therefore shed interesting light on this mechanistic problem. More specifically, one might check whether $[M(CO)_5H{\cdots}CO_2]^-$ is indeed more stable than the reacting species and whether this system is more prone to CO dissociation than $HM(CO)_5^-$ itself. We report here the results of ab initio LCAO-MO-SCF calculations for the $HCr(CO)_5^-$ and $[Cr(CO)_5H{\cdots}CO_2]^-$ systems. We then extend our theoretical study to a preliminary analysis of the insertion reaction by considering possible intermediates for this reaction and discussing their relative energies in terms of electronic requirements.

Computational Details

The SCF calculations were carried out with the ASTERIX system of programs[9] using the following basis set: (14,9,6) contracted to (6,4,3) for the chromium atom;[10] (9,5) contracted to (3,2) for the carbon and oxygen atoms;[12] (6,1) contracted to (3,1) for the hydrogen atom.[13] The contracted basis set is minimal for the inner shells and is of double-ζ quality for the valence shells and of triple-ζ quality for the 3d orbitals of chromium. The use of a rather flexible basis set for hydrogen (i.e. triple-ζ + a p polarization function of exponent 0.8) was required in order to account for the partial hydridic character of this atom.

For the $[M(CO)_5H{\cdots}CO_2]^-$ acid–base adduct 1, the square-pyramid geometry of the $Cr(CO)_5$ framework was kept frozen, the Cr–C and C–O bond lengths amounting to 1.86 and 1.15 Å, respectively, and the C–Cr–C angle to 90°. These values are based on the experimental crystal structures of $HCr(CO)_5^-$[5] and $Cr_2(CO)_{10}(\mu\text{-}H)^-$.[14] The H–Cr and H–C distances and the O–C–O and Cr–H–C angles were optimized to 1.88 and 1.15 Å and 134.5 and 170.0°, respectively, while the C–O bond length of CO_2 was fixed at 1.22 Å, as in $Co(salen)CO_2^-$.[15] For the structures of the various formate complexes (vide infra), the $Cr(CO)_5$ and $Cr(CO)_4$ frameworks were again kept frozen with the same geometrical parameters as above, and the geometries of the formate ligand in the η^1 and η^2 bonding modes were set according to known related structures[2a,6,16–18] and to a partial optimization procedure. In 2a, the bond distance between the carbon and the promixal oxygen atom was set to 1.26 Å. The carbon to distal oxygen bond length and the C–H bond length were fixed at 1.21 and 1.11 Å; the Cr–O–C, O–C–O, and O–C–H angles were set to 127, 127, and 122°, respectively. The Cr–O bond was optimized, the optimum value being 2.18 Å. In 3, the chromium to oxygen bond lengths were optimized to 2.29 Å, setting the two C–O bond lengths and the O–C–O angle to 1.285 Å and 117° and keeping the C–H bond length at 1.11 Å. Although the computed values for the optimized Cr–O bond lengths in 2a and 3 are probably slightly too large, they yield the increase expected on going from an η^1 to an η^2 geometry of the formate ligand.[16e,17b]

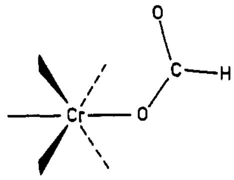


1

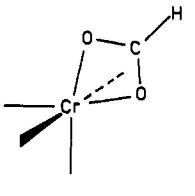
Table I. Atomic Charges and Selected Orbital Populations for the Reactants, Intermediate Adduct, and Product of the CO_2 Insertion Reaction into the Cr–H Bond of $HCr(CO)_5^-$

	$HCr(CO)_5^{-a}$	CO_2^b	$[Cr(CO)_5H{\cdots}CO_2]^-$ (1)[c]	$Cr(CO)_5O_2CH^-$ (**2a**)
Cr	−0.184 (−0.392)		−0.099	+0.186
C_{eq}	+0.307 (+0.294)		+0.273	+0.316
O_{eq}	−0.405 (−0.406)		−0.352	−0.384
C_{ax}	+0.290 (+0.273)		+0.317	+0.298
O_{ax}	−0.415 (−0.423)		−0.379	−0.402
H	−0.298 (−0.008)		+0.171	−0.036
C		+0.728	+0.515	+0.490
O_b		−0.364	−0.605	−0.683
O_t		−0.364	−0.605	−0.579
$3d_{z^2}$	0.587 (0.701)		0.385	0.397
4s	0.197 (0.197)		0.307	0.127
$4p_z$	0.260 (0.291)		0.089	0.071
$3d_\pi$	4.549 (4.578)		4.737	4.664

[a] Experimental geometry. The values in parentheses refer to a stretched Cr–H bond of 1.88 Å, as in the adduct. [b] With the geometry of the adduct. [c] For a linear Cr–H–C unit.



2a



3

In order to check the aptitude of our basis set to account for the geometry of the Cr–H–C unit, preliminary pilot calculations were carried out on the $Cu(PH_3)_3BH_4$ system, which is also an acid–base adduct involving a bridging hydride in a bent Cu–H–B unit, as exemplified by the crystal structures of $Cu(PPh_2Me)_3(BH_4)$[19] and $Cu(triphos)(BH_4)$ (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane).[20] The bent structure (i.e. with a Cu–H–B angle amounting to the experimental value of 121.7° reported in the neutron diffraction study[19b]) was indeed found to be more stable than the linear one by 1.4 kcal/mol.[21] Additional

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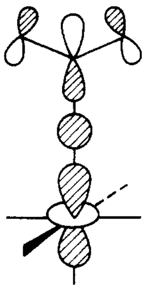
calculations performed on the HCO_2^- formate anion also yielded an optimum C–H bond length in agreement with the one obtained from more refined calculations.[22]

Results and Discussion

We first note that the acid–base adduct $[Cr(CO)_5H\text{---}CO_2]^-$ (**1**) is more stable, at the SCF level, than the $HCr(CO)_5^-$ and CO_2 separated reactants by 8.4 kcal/mol.[23] One may worry however about the effect of neglecting the electron correlation. Previous theoretical studies[27] performed on the acid–base adducts $B_2H_7^-$ and $Al_2H_7^-$, which also involve a bridging hydrogen, have indicated that taking into account the electron correlation does not change the computed stabilization energy by more than a few kcal/mol (the stabilization is increased by 3 and 1 kcal/mol, respectively). The agreement with the experimental value in the case of $B_2H_7^-$ is also rather good.[27a] But we cannot completely exclude that the organometallic analogues behave somewhat differently. CAS SCF calculations carried out on the $HCr(CO)_5^-$ system indicate that the negative charge of the hydride is slightly reduced by the inclusion of the nondynamic correlation effects.[28] This would make the $HCr(CO)_5^-$ system less prone to interact with CO_2 (vide infra). Work is now in progress to test these effects as well as the dynamic correlation effects.[51]

The η^1-C coordination of CO_2 in **1** is not surprising and is easily explained through a strong donor–acceptor interaction (see **4**) between the $d_{z^2} + s_H$ doubly occupied orbital and the empty π^* orbital of CO_2, which is more localized on the central carbon atom than on the terminal oxygen atoms. One has in fact a bonding picture that is similar to the one prevailing for the $Co(salen)CO_2^-$ system, where the occupied d_{z^2} orbital transfers some of its electrons into the π^* orbital of CO_2.[29] But in **1** both the chromium and the hydrogen atoms experience a depopulation to the benefit of the CO_2 moiety (see Table I, where the net atomic charges obtained from a Mulliken population analysis are reported). As in $Co(salen)CO_2^-$, the η^2 geometry is found to be destabilized with respect to the η^1 geometry: Calculations carried out for a 1.15-Å distance between the hydrogen and the C–O bond point to a destabilization of 88 kcal/mol. Although this value would be reduced by optimizing the Cr–H and H–(CO_2) distances, it is too high to make the η^2 coordination mode competitive with the η^1-C one. Here too, orbital interactions are in favor of the η^1-C coordination mode.[29] But they are also reinforced by the electrostatic interactions, at variance with the $Co(salen)CO_2^-$ system, where these electrostatic interactions were found to favor the η^2 coordination mode. In the $HCr(CO)_5^-$ system the hydrogen atom is largely hydridic in character (see Table I) and therefore gives rise to an attractive electrostatic interaction with the positively charged carbon atom of the incoming carbon dioxide. This hydridic character of the hydrogen atom or more generally the negative charge borne by the Cr–H unit (see Table I) also prevents, on electrostatic grounds, a coordination mode involving either one or two oxygen ends.



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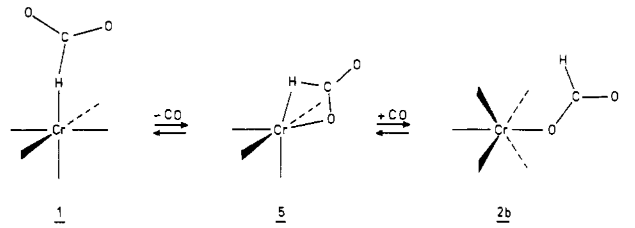

Figure 1. Intermediate structures involved in the most likely reaction pathway for the insertion reaction of CO_2 into the Cr–H bond of the $HCr(CO)_5^-$ system.

Table II. Total and Relative Energies for Characteristic Structures of the CO_2 Insertion Reaction

	tot. energy, au[a]	rel energy, kcal/mol
$HCr(CO)_5^- + CO_2$	−1792.2834	+15.2[b]
$[HCr(CO)_5\text{---}CO_2]^-$ (**1**)	−1792.3076	0
$CO + Cr(CO)_4(\eta^2\text{-}HOCO)^-$ (**5**)	−1792.3028	+3.0
$CO + Cr(CO)_4(\eta^2\text{-}O_2CH)^-$ (3)	−1792.3364	−18.1
$Cr(CO)_5(\eta^1\text{-}O_2CH)^-$ (**2b**)	−1792.3497	−26.4
$Cr(CO)_5(\eta^1\text{-}O_2CH)^-$ (**2a**)	−1792.3561	−30.4

[a] 1 au = 627.7 kcal/mol. [b] Value not corrected by the basis set superposition error. The corrected value is +8.4 kcal mol.[23]

Table III. Dissociation Energy (kcal/mol) of an Equatorial Carbonyl Ligand as a Function of the Cr–H Bond Distance in the $HCr(CO)_5^-$ Complex and as a Function of the Cr–H–C Bonding Angle in the $[Cr(CO)_5H\text{---}CO_2]^-$ Adduct

	d, Å	α, deg	E_{dis}, kcal/mol
$HCr(CO)_5^-$	1.72		29.4
	1.88		28.6
$[Cr(CO)_5H\text{---}CO_2]^-$	1.88	180	23.6
	1.88	160	21.9

In the optimum geometry the CO_2 moiety is eclipsed with respect to the equatorial Cr–CO bonds and bends slightly over the Cr–H bond (the Cr–H–C angle amounts to 170°). In the staggered structure the Cr–H–C angle is slightly more acute (165.6°, owing to less steric hindrance), but the energies of the two isomers are not significantly different. In both cases the potential energy curve is flat, the bending of the Cr–H–C unit leading to a stabilization that is less than 0.5 kcal/mol. This flatness prevents a clear-cut explanation. A possible rationale, somewhat similar to the one put forth to account for the off-axis disposition of the hydrogen atom in the isolobal $Cr_2(CO)_{10}(\mu\text{-}H)^-$ system,[30] lies in a slight increase of the stabilizing interaction provided by the empty $\pi^*_{CO_2}$ orbital. When the Cr–H–C unit bends, the overlap between the oxygen lobe of this orbital and the equatorial lobe of the d_{z^2} orbital would increase. The effect would be small however, owing to the rather long Cr–O distance.

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(21) The geometry of the bent structure for the $Cu(PH_3)_3(BH_4)$ model system was set according to the experimental structure of ref 19b. In the linear structure, the geometry of the two terminal units $Cu(PH_3)_3$ and (BH_4) was kept as in the bent structure, allowing only the relaxation to a C_{3v} symmetry (and keeping the same Cu–H and H–B bond distances as in the bent structure).

(22) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609.

(23) The corresponding total energies are −1792.3076 au for $[Cr(CO)_5H\text{--}CO_2]^-$ in its optimum geometry (see Computational Details), −1604.8729 au for $HCr(CO)_5^-$ in its experimental geometry,[5] and −187.4105 au for CO_2 in its experimental geometry.[24] The energy difference—15.2 kcal/mol—is corrected by the so-called basis set superposition error,[25] which is computed to be 6.8 kcal/mol by the counterpoise method.[26]

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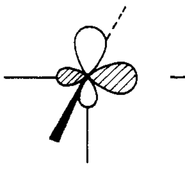
An interesting feature of **1** is the relatively short C–H distance, 1.15 Å, close to the value expected in the formate ligand.[16] The Cr–H bond length is about 0.2 Å longer than that in $HCr(CO)_5^-$.[5] This suggests that in the adduct the HCO_2 moiety has gained much of the character of the formate product. The corresponding Mulliken population analyses are consistent with this proposal: The atomic charges of the carbon and oxygen atoms in the adduct and in the formate ligand are quite similar (see Table I). In particular, the oxygen atoms in both systems are much more negative than in CO_2 alone and the carbon atom is less positive. This results merely from the charge-transfer interaction **4**, which populates the $\pi^*_{CO_2}$ orbital at the expense of the $3d_{z^2}$ and $4p_z$ chromium orbitals and the 1s hydrogen orbital.

That the CO_2 adduct **1** is much like the final formate product suggests that the end of the insertion process should not be characterized by an intricate change in the internal geometry of the HCO_2 moiety but rather involve a gradual shift of this moiety toward its location in the product. There are of course various pathways for this rearrangement, and we have not yet carried out a complete determination of the corresponding reaction paths and transition states. But some useful information about this process could be obtained by carrying out calculations on the discrete structures that are possibly involved.

A reasonable reaction channel is sketched in Figure 1. It involves the dissociation of CO as experimentally proposed,[3-6] the bonding of an oxygen atom to the open coordination site to give the η^2 structure **5**, in which both the hydrogen and the oxygen atoms are bound to the chromium atom, and the final relaxation of **5** to **2b**, which is the trans isomer of **2a**. The corresponding energy results are given in Tables II and III. As seen from Table III, both the CO_2 coordination to the hydride and the subsequent bending of the HCO_2 unit from 180 to 160° decrease the dissociation energy of the cis carbonyl ligand,[31] thus pointing to a cis-labilizing effect, as experimentally expected[4] (the dissociation of a trans CO ligand is also found to be slightly more endothermic, 28.1 kcal/mol instead of 23.6 kcal/mol). The destabilization of **5** + CO with respect to **1** is small, amounting to 3.0 kcal/mol only.[33] Whether or not **5** is the actual transition state is difficult to assess at this stage of our calculations. But the above results indicate that this type of structure is most likely involved in the process. It is in fact made accessible by the CO dissociation, which provides a C_{2v} $Cr(CO)_4$ fragment having the orbitals of right symmetry to interact in a η^2 fashion with the HCO_2^- ligand. For the $Cr(CO)_4$ fragment one finds,[30,34] above a set of three doubly occupied orbitals that are reminiscent of the t_{2g} orbitals, a b_2 (**6**) and an a_1 (**7**) orbital, which are both empty. Their possible interacting partners in the formate ligand, sketched in **8**–**10**, are all occupied. Note that **10** is characterized by an out-of-phase combination between the p components on the oxygen atoms and the s component on the hydrogen atom.[35] It is this particular shape that will play the key role in the stabilization of the η^2-H,O structure **5** since it allows, in addition to the two-electron stabilizing interaction **11** between **7** and **8**, another one **12** between **6** and **10**. In contrast, should the hydrogen be substituted by a methyl group, then the orbital corresponding to **10** in the resulting acetate ligand would be **13**. In this case, the presence of the p component arising from the CH_3 substituent would reduce the overlap with **6** and hence lead to a relatively greater destabilization of the η^2 structure **5**. This may therefore explain why an associative mechanism prevails for the CO_2 insertion into the metal to methyl bond of $M(CO)_5CH_3^-$ systems (M = Cr, W).[7,8,36,37] One has in fact here a situation that is akin to the one observed for the H–H and C–H oxidative-addition reactions and that has been rationalized along the same lines by Saillard and Hoffmann.[38]



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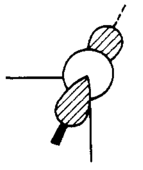

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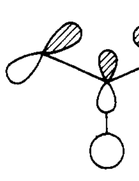

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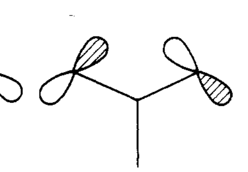

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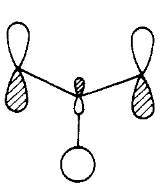

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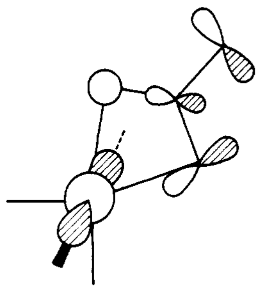

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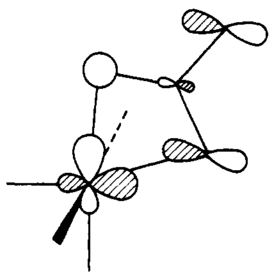

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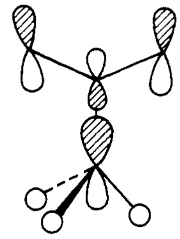

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The reader may have also noticed that **2b** is not the isomer that is experimentally observed.[2a,6,16] We indeed find **2a** more stable than **2b** by 4 kcal/mol (see Table II). **2a** might be easily reached from **2b** through a rotation of the formate ligand around the C–O bond, the barrier to overcome amounting to 2.3 kcal/mol.[39] But this rotation might also occur while the hydrogen atom in **5** is pulled off. The result of this concerted process would then be the η^2 structure **3**, which we find lower in energy than **5** (see Table II). This is not surprising since **6** interacts more strongly with **9** than with **10**. Whether **3** actually belongs to the reaction path of the reactive channel or is a "dead end" stationary point of the potential hypersurface has still to be established through more refined calculations.

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(31) We are well aware of the fact that the absolute values computed for the dissociation energy of the CO ligand may not be reliable at the SCF level.[32] Yet, their relative ordering is probably meaningful since the correlation energy and the basis set corrections should not vary very much on going from one $[Cr(CO_5)H{\cdots}CO_2]^-$ structure to another one.

(32) (a) For a calculation including correlation energy on the closely related $Cr(CO)_6$ system, see for instance: Moncrieff, D.; Ford, P. C.; Hillier, I. H.; Saunders, V. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1108. (b) Other references to theoretical calculations of M–CO bond dissociation energies may be found in: Ziegler, T.; Tschinke, V.; Ursenbach, C. *J. Am. Chem. Soc.* **1987**, *109*, 4825.

(33) For the geometry of the $Cr(HCO_2)$ moiety in **5**, the Cr–H and Cr–O bond lengths were set to 1.88 and 2.29 Å, as in **1** and **3**, respectively. The bond lengths of the HCO_2 unit in **3** were kept, except for the length of the noncoordinated C–O bond, which was set to 1.22 Å. The H–C–O and O–C–O angles were set to 111 and 127°, respectively.

(34) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

(35) This results from a second-order mixing of $\pi^*_{CO_2}$ into the antibonding combination between π_{CO_2} and s_H.

(36) Darensbourg, D. J.; Rokicki, A. *J. Am. Chem. Soc.* **1982**, *104*, 349.

(37) Darensbourg, D. J.; Kudaroski, R. *J. Am. Chem. Soc.* **1984**, *106*, 3672.

(38) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(39) For the $Cr(CO)_5(HCO_2)^-$ system with a formate ligand rotated by 90° and a Cr–O bond length of 2.00 Å, the total energy amounts to −1792.3406 au, to be compared with −1792.3443 au for **2b** and −1792.3506 au for **2a**.

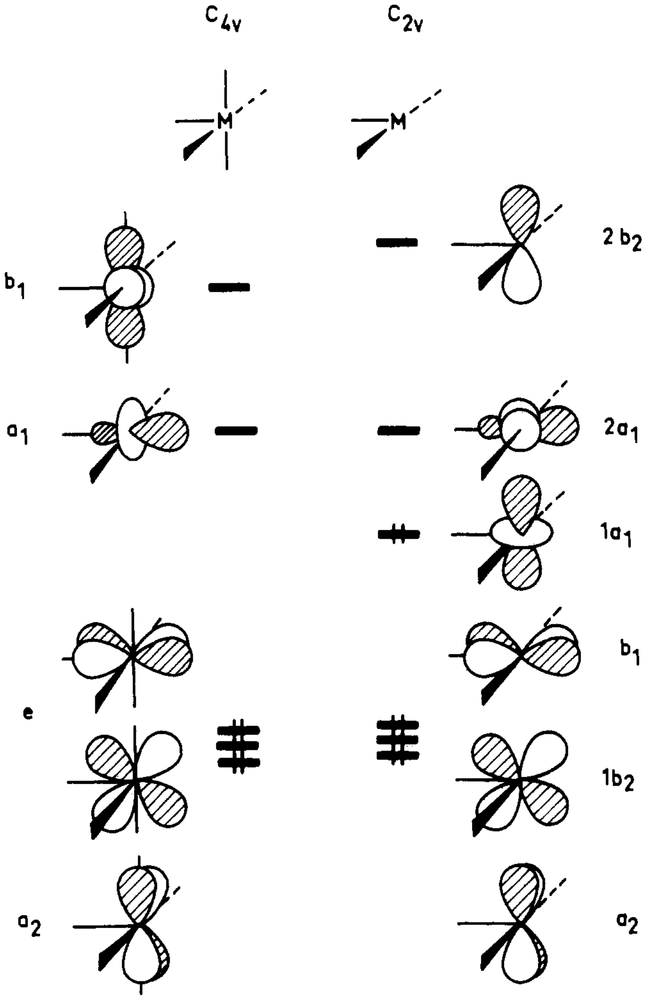
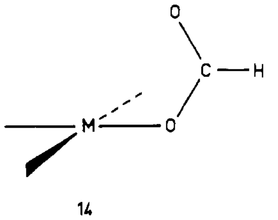


Figure 2. Valence orbitals of the d^6 C_{4v} ML_5 and d^8 C_{2v} ML_3 fragments.[43]

One might also wonder why the CO_2 insertion reaction or its inverse, the decarboxylation reaction of the formate product, seems to involve an ancillary ligand dissociation in the case of the $HCr(CO)_5^- + CO_2 \rightleftarrows Cr(CO)_5(HCO_2)^-$ equilibrium and apparently not for square-planar d^8 $ML_3(HCO_2)$ complexes such as $(PPh_3)_3Rh(HCO_2)$[40] and various $HPtL_2(HCO_2)$ systems,[16a,41] which have the formate ligand in the upright conformation **14**.[16a,40]



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This difference is even more puzzling if one refers to the isolobal analogy between the d^6 C_{4v} ML_5 and d^8 C_{2v} ML_3 fragments.[42,43] As shown in Figure 2, these two systems are characterized by three occupied orbitals that can be used for eventual π bonding and by a low-lying empty orbital of a_1 symmetry. This latter orbital (d_{z^2} in the case of $HCr(CO)_5^-$) is therefore ready to accommodate an incoming σ-donor ligand, e.g. the formate ligand in $Cr(CO)_5(HCO_2)^-$ and $(PPh_3)_3Rh(HCO_2)$. There is one difference, however: in the d^8 ML_3 fragment, a second low-lying empty orbital, of b_2 symmetry, is present (see Figure 2). This is precisely what is needed in order to assist the η^2-H,O structure or the η^2-O,O structure. On the other hand, no such orbital exists in the $Cr(CO)_5^-$ fragment; it will be only provided by the loss of an equatorial CO. Also, the absence of a similar low-lying empty orbital in the d^{10} tetrahedral $(triphos)Cu(HCO_2)$ complex (or in the d^{10} C_{3v} $(triphos)Cu^+$ fragment), combined with the relative rigidity of the triphos ligand and the low propensity of the copper to form hydride, which have been already noted, might well account for the fact that this system does not undergo decarboxylation at room temperature.

At this point we may digress somewhat and note that the decarboxylation reaction of the metalloformate complex $Cr(CO)_5(HCOO)^-$ or of its isomer the hydroxycarbonyl complex $Cr(CO)_5(COOH)^-$ should bear some resemblance to the decarboxylation reaction of formic acid, HCOOH, owing to the isolobal analogy between $Cr(CO)_5^-$ and H.[42] It has been recently shown that the HCOOH decarboxylation reaction, which has a rather high energy barrier in the gas phase, is helped by the mediation of water, which enters the transition state and acts as a proton relay.[44] The structure of the transition state is therefore changed from a four-membered ring to a less energy-demanding six-membered ring. Interestingly, the assistance of a base bearing a hydrogen atom has also been proposed as a possible reaction pathway for the hydroxycarbonyl decarboxylation reaction both in the gas phase[45] and in solution.[46,47] We can make use of the above mentioned isolobal analogy to account for this proposal. In the case of the metalloformate decarboxylation, the ancillary ligand dissociation, by creating an empty orbital of b_2 symmetry to stabilize the Cr--H--C--O four-membered ring itself, will provide another kind of assitance.

Conclusion

From this study it therefore appears that the CO_2 insertion reaction into the metal–hydride bond of $Cr(CO)_5H^-$ seems to involve an acid–base adduct that is more stable than the reactants by about 8 kcal/mol. The geometry optimization of the HCO_2 unit in this adduct points to an η^1-C coordination of the carbon dioxide to the hydrido carbonyl complex. A rearrangement of this unit into an η^2-O,H formate structure, coupled with an ancillary CO dissociation, is found to be of low-energy cost and is likely involved in the actual insertion process.[48,49] The analysis of the corresponding orbital interactions provides additional

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(40) Strauss, S. H.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1979**, *174*, C59.

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(45) Lane, K. R.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 7187.

(46) Catellani, M.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 566.

(47) Trautman, R. J.; Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 2355.

(48) Exploratory calculations carried out for the $HCr(CO)_4(\eta^2\text{-}CO_2)^- + CO$ system point to a high destabilization with respect to **1**, therefore precluding as a likely alternative the CO_2 coordination to an unsaturated $HCr(CO)_4^-$ intermediate obtained from CO dissociation.

(49) After this work was submitted, a theoretical study—somewhat complementary to ours—of the CO_2 insertion into the Cu–H bond of $Cu(PH_3)_2H$ appeared.[50] From this study, in which the geometries of the reactants and products were optimized with the energy gradient method and the geometry change during the reaction was optimized through a parabolic fitting of the total energies, the transition state appears to have some η^2-H,O character, although the Cu–O distance is rather long (2.45 Å vs 1.6 Å for the Cu–H bond length). The importance of charge-transfer interaction from $Cu(PH_3)_2H$ toward CO_2 is stressed in addition to some electrostatic interaction between the metal center and the oxygen end of the CO_2 moiety. The energy difference between the two rotational isomers of the $(\eta^1\text{-}O_2CH)Cu(PH_3)_2$ formate complex is found to be greater than that in the $(\eta^1\text{-}O_2CH)Cr(CO)_5^-$ system (13–14 kcal/mol vs 4 kcal/mol).

(50) Sakaki, S.; Ohkubo, K. *Inorg. Chem.* **1988**, *27*, 2020.

(51) **Note Added in Proof.** Preliminary CAS SCF calculations carried out for the acid–base adduct $[Cr(CO)_5H\cdots CO_2]^-$ and for the two reactants separated by 50 Å have indicated that the inclusion of the most important σ and π nondynamic correlation effects does not completely offset the stabilization computed at the SCF level: The decrease of the stabilization energy amounts to 3.1 and 3.6 kcal/mol for the σ and π correlation effects, respectively, when the SCF-optimized geometry of the Cr–H–C unit is used. Optimizing this geometry at the CAS SCF level should further reduce these values.

support for this proposal and accounts for the fact that the insertion into a metal-alkyl bond occurs through a different mechanism.

Acknowledgment. Calculations were carried out on the IBM 3081 computer of the Centre de Calcul de Strasbourg-Cronenbourg. The permanent affiliation of C.B. is the Departament de Quimica, Universitat de Barcelona, P. Imperial Tarraco 1, 43005 Tarragona (Catalunya), Spain.

Registry No. $HCr(CO)_5^-$, 18716-81-9; CO_2, 124-38-9.

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Photophysical Investigation of Palladium(II) Ortho-Metalated Complexes

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Syntheses and structural characterizations of four complexes of Pd(II) with ortho-metalated 2-phenylpyridinate (ppy^-) are reported. These complexes include a parent dimer, $[Pd(ppy)Cl]_2$, and three derivative monomers, [Pd(ppy)(bpy)]Cl, [Pd(ppy)(en)]Cl, and [Pd(ppy)(CO)Cl], where bpy = 2,2′-bipyridine and en = ethylenediamine. Photophysical characterizations of these species indicate low-energy absorption bands (~360 nm) and emission bands at 77 K (~460 nm) that are assigned to transitions localized on the ppy^- ligand. Some evidence for low-energy charge-transfer states is found in trends in luminescence lifetimes.

Introduction

Ortho-metalated complexes of palladium(II) have long been recognized in the literature,[1-8] yet there is an apparent lack of photochemical and photophysical data reported for these complexes.[9] We have prepared four palladium(II) complexes, each of which contains the ortho-metalating ligand 2-phenylpyridinate (ppy^-). Ortho-metalates of palladium were chosen for our investigation in order to explore the effects of metal-carbon σ bonds on the low-energy excited states of Pd(II) complexes. Investigations of these Pd(II) complexes are being carried out in order to establish whether or not low-energy charge-transfer excited states are present and to evaluate their potential use in photoinduced electron- and energy-transfer schemes.

Photophysical descriptions of several palladium(II) ortho-metalated azobenzene complexes[10] indicate that the photophysics of these systems is predominantly ligand-localized in character. Luminescence lifetimes of these complexes are short in room-temperature fluid solutions (<1 ns) and are characterized as singlet intraligand fluorescence emissions. Photophysical characterizations of rhodium(III), iridium(III), and platinum(II) compounds containing the ortho-metalating ligand ppy^- have been reported previously.[11-14] $[Rh(ppy)_2Cl]_2$ has a low-energy charge-transfer feature in the absorption spectrum (395 nm); however, low-temperature emission and luminescence lifetime data indicate that the emission originates from a ligand-localized excited state. The analogous $[Ir(ppy)_2Cl]_2$ dimer also exhibits a low-energy charge-transfer absorption (435 nm), and in this case the emission has been assigned as metal-to-ligand charge-transfer (MLCT) emission. Photophysical results for platinum(II) complexes that contain ppy^- as a ligand indicate that the emitting state is MLCT.[13-14] Since Pd(II), like Rh(III), is difficult to oxidize, one might expect to observe MLCT transitions in the absorption spectra of palladium-ppy^- complexes while the emission may originate from ligand-localized states. On the other hand, palladium(II) being a d^8 transition metal may alter the ground-state energies enough that new MLCT states would be observed. Current results indicate that coordination to iridium(III) and rhodium(III) by the anionic carbon of an ortho-metalating ligand enhances the electron density about the metal center.[11] This suggests that ortho-metalating ligands coordinated to Pd(II) may promote metal-to-ligand charge-transfer transitions via σ donation of electron density to the palladium metal center.

We have prepared four palladium-centered complexes. Common to each species is the anionic 2-phenylpyridinate ligand. In the work presented here we report on our initial investigation of the photophysical properties of these ortho-metalated Pd(II) complexes (bpy = 2,2′-bipyridine, en = ethylenediamine): $[Pd(ppy)Cl]_2$ (I); [Pd(ppy)(bpy)]Cl (II); [Pd(ppy)(en)]Cl (III); [Pd(ppy)(CO)Cl] (IV).

Experimental Section

A. Syntheses. Bis(2-phenylpyridinato-C^2,N')bis(μ-chloro)dipalladium(II). Li_2PdCl_4 (0.670 g, Aldrich) was dissolved in methanol, and to this solution was added 420 μL of C-protonated 2-phenylpyridine (ppy). The brown solution immediately lightened upon addition of ppy, and after 24 h a yellow-green solid was collected on a glass frit. This material was washed with dichloromethane. The solid was then dissolved in *N,N*-dimethylformamide and the solution filtered. Evaporation of the DMF produced the bright yellow $[Pd(ppy)Cl]_2$ powder (0.5026 g, 66% yield). This yield correlates well with previously reported values for the synthesis of this compound.[6] Recrystallization of the $[Pd(ppy)Cl]_2$ powder from dichloromethane and hexanes provided material suitable for elemental analysis.

Anal. Calcd for $Pd_2C_{22}H_{16}N_2Cl_2$: C, 44.63; H, 2.72; N, 4.73. Found: C, 44.42; H, 2.72; N, 4.84.

(2-Phenylpyridinato-C^2,N')(2,2′-bipyridine)palladium(II) Chloride. 2,2′-Bipyridine (0.1075 g, Aldrich) was added to a dichloromethane solution of $[Pd(ppy)Cl]_2$ (0.0610 g, 400 mL) and stirred at ambient temperature for 48 h. The yellow precipitate was removed and washed with diethyl ether. The remaining solid was dissolved in 300 mL of hot methanol and the solution filtered. Isobutyl alcohol (100 mL) was added, and the solvents were allowed to evaporate slowly. The yellow microcrystals of [Pd(ppy)(bpy)]Cl were collected, dried in vacuo, and weighed (0.0708 g, 76% yield).

Anal. Calcd for $PdC_{21}H_{16}N_3Cl{\cdot}CH_2Cl_2$: C, 49.19; H, 3.37; N, 7.82. Found: C, 49.94; H, 3.20; N, 7.93.

(2-Phenylpyridinato-C^2,N')(ethylenediamine)palladium(II) Chloride. Ethylenediamine (64.5 μL, Aldrich) was added to a dichloromethane solution of $[Pd(ppy)Cl]_2$ (0.0720 g, 500 mL). The yellow solution lightened and formed a white precipitate within several minutes. This reaction mixture was stirred at room temperature for 4 h. The white flocculent product was collected on a glass frit and washed with di-

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