Table VII. Coupling Constants ^2J(H-M) (Hz) for the Dimethylthallium and Methylmercury Complexes

compd	^2J(H-Tl)	^2J(H-Hg)	ref (MeHg$^+$ compds)
Me_2TlL^1	400	160	49
Me_2TlL^2	417	173	49
Me_2TlL^3	417	172	24
Me_2TlL^4	417	171	24
Me_2TlL^5	419	190	49
Me_2TlL^6	423	175	51
Me_2TlL^9	426	178	51
Me_2TlL^{10}	435	182	51

relationships observed in the case of methylmercury also hold for dimethylthallium(III). In order to answer this question, we have made use of the fact that most of the methylmercury(II) complexes of the ligands used in the present study have already been studied and the corresponding values of ^2J(H-Hg) determined.[49,51] In Figure 6 these values are plotted against the values of ^2J(H-Tl) for complexes of the same ligands with Me_2Tl^+ (Table VII). Least-squares analysis shows the correlation among these data to be poor ($r = 0.714$) if the totality of the points are taken into account but very good ($r = 0.9915$) if the data for the ligand HL^5 are omitted. Though the number of systems considered is small, it would be desirable to investigate a wider range of complexes of different structural ligands, Figure 6 suggests that ^2J(H-Tl) and ^2J(H-Hg) are affected in the same way by the same ligands. The exceptional case of Me_2TlL^5 may be due to the second bond being Tl-O in Me_2TlL^5, whereas it is Tl-N in the other complexes considered.

Acknowledgment. We gratefully acknowledge the CAICYT (Spain) for financial assistance and Prof. A. Macias for ORTEP drawings.

Registry No. HL^1, 108-98-5; HL^2, 2637-34-5; HL^3, 1450-85-7; HL^4, 35071-17-1; HL^5, 33486-07-6; HL^6, 60-56-0; HL^7, 583-39-1; HL^8, 96-53-7; HL^9, 149-30-4; HL^{10}, 2382-96-9; Me_2TlL^1, 16834-15-4; Me_2TlL^2, 114928-71-1; Me_2TlL^3, 114944-20-6; Me_2TlL^4, 114928-72-2; Me_2TlL^5, 114928-73-3; Me_2TlL^6, 114928-74-4; Me_2TlL^7, 114928-75-5; Me_2TlL^8, 114928-76-6; Me_2TlL^9, 114928-77-7; Me_2TlL^{10}, 114928-78-8; Me_2TlOH, 53759-11-8; ^{205}Tl, 14280-49-0.

Supplementary Material Available: A table of thermal parameters (1 page); a listing of observed an calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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Theoretical Investigation of the Platinum Ketene Complex $Pt(PR_3)_2(CH_2{=}C{=}O)$ and Carbene Complex $Pt(PR_3)_2(CH_2)(CO)$

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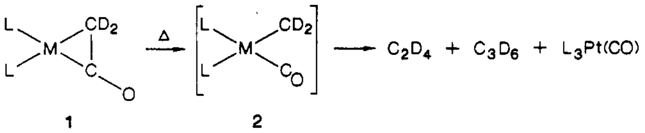
An ab initio MO study has been carried out on the structure and energetics of the platinum ketene complex $Pt(PR_3)_2(CH_2{=}C{=}O)$, the carbene carbonyl complex $Pt(PR_3)_2(CH_2)(CO)$, and the possible transition state connecting them, taking R = H as the model. The most stable ketene complex has been calculated to have the η^2(C-C) square-planar structure with the CH_2 group perpendicular to the molecular plane. Comparison between η^2(C-C) and η^2(C-O) coordination and between perpendicular CH_2 and in-plane CH_2 orientations has been made. The carbene carbonyl complex has been found to have a square-planar structure with its CH_2 group in the molecular plane, stabilized by the strong CH_2 π-Pt π interaction. The transition state connecting the ketene complex and the carbene carbonyl complex has a structure in which CH_2 is twisted halfway from the perpendicular to the in-plane conformation. The possibility of the existence of the carbene carbonyl intermediate in thermolysis of the ketene complex is discussed as well.

I. Introduction

Carbon-carbon bond formation and cleavage is one of the central objectives of modern catalytic chemistry. The reaction of transition-metal ketene complexes[1] is currently drawing considerable attention in this regard, as consisting of elementary steps[2] relevant to models for heterogeneous[3] and homogeneous carbon monoxide reduction.[4] Recently Miyashita et al.[5] have synthesized unsubstituted ketene complexes $M(PPh_3)_2(CH_2{=}C{=}O)$ (**1**, M = Ni, Pd, and Pt) and have reported thermolysis of these complexes that produced hydrocarbons such as C_2H_4 and C_3H_6. To explain this reaction, they proposed a carbene carbonyl intermediate, **2**. Although there exist several examples[1d,2,6]



1 **2**

L = PPh_3

[†] IMS.

[‡] Mitsubishi Chemical Industries.

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for the reverse addition or insertion of CO to $M{=}CH_2$ forming ketene complexes, little is known about the intramolecular C—C cleavage and the resultant carbene intermediate.

In this paper, we present ab initio MO theoretical investigation on geometries and energies of the ketene complex, the carbene carbonyl complex, and the possible transition state connecting the two, where the ligand L is PH_3 as a model for PPh_3.

II. Method of Calculation

We optimized all the degrees of freedom with the restricted Hartree–Fock (RHF) energy gradient method, except in search of the transition state where the geometries of PH_3's were fixed so as to freeze their free rotation. For acquisition of better energetics, a frozen core second-order Møller–Plesset perturbation (MP2) calculation was carried out at the RHF optimized geometries. We employed the relativistic effective core potential approximation[7] for Pt in most calculations, considering up to 5p electrons as the core with the valence double-ζ orbitals of Noell and Hay.[7a] In a few cases calculations were carried out considering only up to 4d electrons as the core.[7b] We used for C, O, and H the 3-21G[8a] basis set and for P and H of PH_3 the STO-2G[8b] basis set. We used the GAUSSIAN80 program[9] incorporated with the effective core potential program.

III. Ketene Complex

The optimized equilibrium geometry of the ketene complex **3** is shown in Figure 1. It has a planar structure with C_s symmetry. The geometry was at first optimized with the C_s constraint, and a small deviation from the C_s-constrained structure toward tetrahedral was found to create a force that restored the planar structure. A local minimum in a tetrahedral structure was also searched for by gradient optimization. First, the one-point calculation with the ketene rotated by 90° from the optimized square-planar complex gave an energy higher by 25 kcal/mol than the optimized planar structure, and moreover the optimization from this tetrahedral geometry led to dissociation to CH_2CO and $Pt(PH_3)_2$, indicating that the tetrahedral ketene complex is by far less stable than the planar complex and is not an equilibrium structure. Though the X-ray structure has not been established yet, the planar equilibrium structure we predict theoretically is supported by a recent ^{31}P NMR experiment where two phosphorus atoms in **3** are found to lie in different chemical environments.[5c]

The preference of the planar structure can be understood by examining the shape of d orbitals of the $Pt(PH_3)_2$ fragment that donate electrons to the π^*_{CC} orbital. In the planar approach, the back-donating d orbital mixed with the two PH_3 lone pair orbitals in an antibonding fashion is high in energy and is extended spatially toward the approaching C=C bond, both factors contributing to strong back-donation to π^*_{CC}. On the other hand, in the perpendicular approach, the back-donating d orbital is low in energy and is of pure d character, resulting in a weaker interaction.

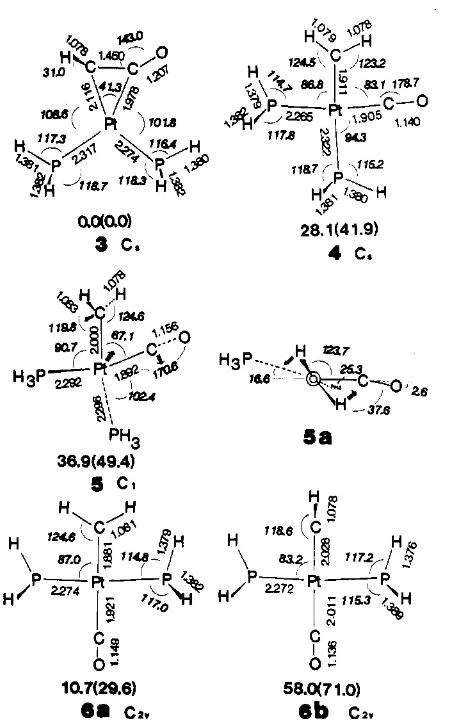
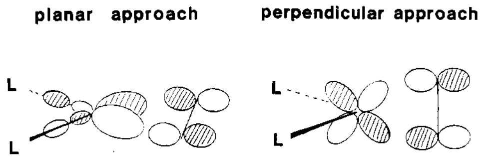


Figure 1. Geometries (in Å and deg) of $Pt(PH_3)_2(CH_2{=}C{=}O)$ (**3**), *cis*-$Pt(PH_3)_2(CH_2)(CO)$ (**4**), transition state **5**, and two forms of *trans*-$Pt(PH_3)_2(CH_2)(CO)$ (**6**), fully optimized at the RHF level. Arrows in **5** show the approximate reaction coordinate vector. **5a** is viewed along the Pt–CH_2 axis of **5**. Energies are in kcal/mol at the MP2 level and at the RHF level in parentheses, relative to **3** whose MP2 energy is −837.740 83 and RHF energy is −837.149 66 hartrees.



A similar detailed analysis has been presented by Albright et al.[10] for the $L_2Ni(C_2H_4)$ system, where C_2H_4 is isolobal to CH_2CO.

The ketene complex **3** shows two structural features: (i) a rather long C–C distance of 1.450 Å (cf. 1.296 Å of free ketene, optimized with the same method) and (ii) a bent ketene unit with a CCO angle of 143.0° and a CCH_2 angle of 149.0°. These indicate that the C=C double bond is virtually transformed into a single bond, which is consistent with "significant single-bond character" for the CC bond in $Pt(PPh_3)_2(CH_2{=}CH_2)$ as experimentally found by Nyburg et al.[11] The calculated CCO angle agrees well with the 145.0° value found for η^2(C–C)-$CpMn(CO)_2(Ph_2C{=}C{=}O)$.[12] Pt–C distances of 2.116 and 1.978 Å also agree with experimental values in related complexes,[13] for instance, 2.116 and 2.106 Å in $Pt(PPh_3)_2(CH_2{=}CH_2)$.[11]

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Table I. Mulliken Population Analysis for Valence Electrons on Platinum Atom[a]

	$Pt(PH_3)_2(CH_2CO)$ (3)	*cis*-$Pt(PH_3)(CHNH_2)Cl_2$[b]	$Pt(PH_3)_2(CH_2)(CO)$ (6)
d_{xy}	1.898	1.882	1.911
d_{yz}	1.969	1.984	1.900
d_{xz}	1.943	1.982	1.911
$d_{x^2-y^2}$	1.361	1.000	1.171
d_{z^2}	1.879	1.955	1.894
s	0.810	0.808	0.777
p_x	0.510	0.422	0.497
p_y	0.487	0.557	0.380
p_z	0.056	0.245	0.712

[a] Both planar molecules are in the *xy* plane, with the *x* axis pointing to 45° from the bisector of the CPtC toward the terminal C in 3 and to the direction of the carbene C in *cis*-$Pt(PH_3)(CHNH_2)Cl_2$ and 6. Five d functions (excluding a spherical component) are used for this table only. [b] Geometrical parameters are taken from experiments[14] for *cis*-$Pt(PPh_3)(CHN(CH_3)_2Cl_2$.

In Table I we show the results of a Mulliken population analysis for this compound as well as for square-planar *cis*-$Pt(PH_3)(CHNH_2)Cl_2$ as a model for *cis*-$Pt(PPh_3)(CHN(CH_3)_2)Cl_2$,[14] which is generally considered to be a typical d^8 system. The population in the most unstable of the Pt d orbitals, $d_{x^2-y^2}$, for 3 is 1.361, indicating that a substantial back-donation is taking place from the Pt $d_{x^2-y^2}$ orbital to the π^*_{CC} orbital. Though this value is not as small as 1.000, the Pt $d_{x^2-y^2}$ population of d^8 *cis*-$Pt(PH_3)(CHNH_2)Cl_2$, one might formally consider 3 as a d^8-like rather than d^{10}-like complex, which is consistent with experimentally observed plantinacyclopropane-like character.[5] A similar d^8 interpretation has been proposed by Albright et al.[10] for $Ni(CH_2{=}CH_2)L_2$, where L is a neutral ligand.

η^2(C–O) vs η^2(C–C) Coordination. There exist two coordination modes for transition-metal ketene complexes: the η^2(C–O) mode for early transition metals and the η^2(C–C) mode for late transition metals. For examples, well-established X-ray structures are known in the η^2(C–O) mode for Zr,[15] Ti,[16] and V[17] and in the η^2(C–C) mode for Mn.[12,18] Spectroscopic evidences for the η^2(C–C) mode have been reported for Fe,[2] Ni,[5a,19] Pd,[5c] and Pt.[5b]

A qualitative general consideration and a model extended Hückel calculation on η^2(C–O)-$Cp_2V(CH_2CO)$[17] and η^2(C–C)-$[CpFe(CO)_2(CH_2CO)]^+$ suggest that the essential orbital interactions in the η^2(C–C) mode would be $d\pi \rightarrow \pi^*_{C-C}$ back-donation and $\pi_{CC} \rightarrow$sp (and d if available) donation, while in the η^2(C–O) mode the essentials are $d\pi \rightarrow \pi^*_{CO}$ back-donation, $\pi_{CO} \rightarrow$sp (and d if available) donation, and supplemental oxygen lone pair→d donation. The last interaction, which exists only in the η^2(C–O) mode, is favorable particularly for electron-poor metals. This strong donative interaction would give preference to η^2(C–O) coordination in early-transition-metal complexes. For intermediately electron-rich metals a competition between the two modes is expected. Indeed for $Cp_2W(CH_2CO)$ Miyashita et al. have found spectroscopic evidence for the interconversion between the two modes.[5c]

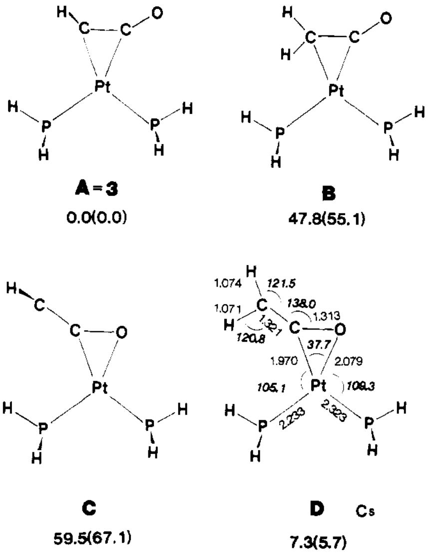

Figure 2. The optimized geometry of η^2(C–O) form of $Pt(PH_3)_2(CH_2{=}C{=}O)$ with in-plane CH_2, D, and the relative energies of various modes of coordination in kcal/mol at the MP2 level and at the RHF level in parentheses.

Table II. Energetics along Approximative Dissociation Path for $Pt(PH_3)_2(CH_2CO) \rightarrow Pt(PH_3)_2 + CH_2CO$

	ΔE, kcal/mol	
R,[a] Å	RHF	MP2
1.915[b]	−5.0	−12.7
2.05	−1.7	−12.6
2.25	+8.7	+5.2
2.50	+13.7	+4.0
2.75	+9.8	+2.7
∞	0	0

[a] Distance between Pt and the center of C–C bond. All the other geometrical parameters are optimized at the RHF level. [b] The RHF optimized geometry of the complex 3.

As an example of late-transition-metal complexes, the present $Pt(PH_3)_2(CH_2CO)$ with square-planar geometry could exist a priori in four possible modes of coordination: A, η^2(C–C) with perpendicular CH_2; B, η^2(C–C) with in-plane CH_2; C, η^2(C–O) with perpendicular CH_2; and D, η^2(C–O) with in-plane CH_2. The optimized geometry of the η^2(C-O) complex D is shown in Figure 2. In Figure 2 we also compare the relative stability among the four modes. The geometries of B and C, with a C_s symmetry, are derived from those of A and D, respectively, by placing the CH_2 group in the planar and perpendicular position, respectively. The η^2(C–C) complex is more stable than the η^2(C–O) complex. In the η^2(C–C) complex the perpendicular CH_2 is preferred strongly, and in the η^2(C–O) complex the in-plane CH_2 is preferred strongly as well. These preferred structures are consistent with the ordering of the electron-accepting vacant orbitals of ketene. The two lowest vacant orbitals are the π^*_{CO} orbital in the plane of the CH_2 group and the π^*_{CC} orbital perpendicular to the CH_2 plane, convenient to D- and A-type coordination, respectively. The larger stability of A compared with D is ascribable to the fact that the oxygen lone pair would exert a larger exchange repulsion with Pt d electrons, making D less stable. The possibility of interconversion between A and D would be a subject of future study.

Binding Energy and Dissociation Barrier of the Ketene Complex. In order to obtain a reasonable estimate for the binding energy and the dissociation barrier

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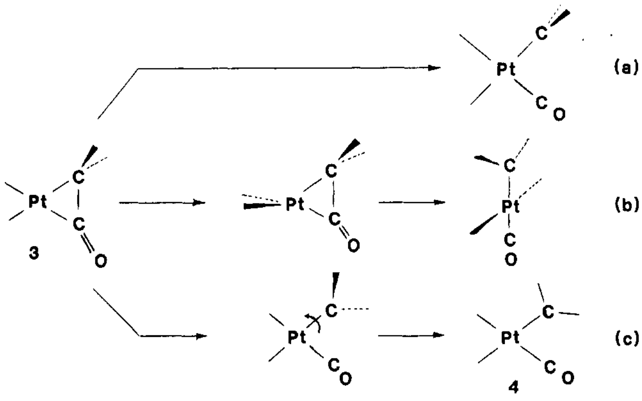
Scheme I

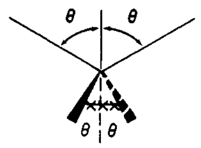


height of ketene from the ketene complex **3**, $Pt(PH_3)_2(CH_2O) \rightarrow Pt(PH_3)_2 + CH_2CO$, we have followed the approximate path of dissociation reaction at the RHF level, starting from the complex **3**, by taking several fixed values of the distance between Pt and the center of the C–C bond and optimizing all the remaining geometrical parameters at each fixed Pt–CC distance. The MP2 energies are calculated at the RHF optimized geometries. The results are shown in Table II. The electron correlation makes a substantial difference in the overall energetics. Focusing on the more reliable MP2 results, one finds that the binding energy of the ketene ligand in **3**, $E(R = \infty) - E(R = 1.915\ \text{Å})$, is about 13 kcal/mol and the barrier required to overcome for dissociation of **3** is about 19 kcal/mol. There is no reliable experimental result for either quantity.

IV. Carbene Intermediate

Now let us search for a carbene carbonyl intermediate.[20] Starting from the ketene complex **3**, three possible modes of C–C cleavage, shown in Scheme I, have been examined. First, the least motion C–C cleavage maintaining the C_s symmetry, path a, resulted in a monotonic energy increase, and there was no stable minimum. Second, path b was tested with rotation of the ketene to give an unstable tetrahedral structure followed by the C–C cleavage to give *trans*-$Pt(PH_3)_2(CH_2)(CO)$. The optimized structure of *trans*-$Pt(PH_3)(CH_2)(CO)$ (**6a**), shown in Figure 1, has an energy only 11 kcal/mol higher than that of the ketene complex **3** at the MP2 level. However, this path has been found to have a very high barrier and must be excluded. This is because the path is symmetry-forbidden in the same manner as the trans addition of H_2 to $Pt(PH_3)_2$.[21] Finally, the direct C–C cleavage accompanied by the CH_2 rotation, path c, gave a stable square-planar cis carbene complex, **4**. The relative energy of the cis carbene complex **4** is 28 kcal/mol (at the MP2 level) above the ketene complex **3**.

The optimized geometry of **4** is shown in Figure 1. The most interesting feature of this square C_s complex is that the CH_2 group lies in the molecular plane. The planarity has been confirmed by two additional calculations. The complete optimization without symmetry constraints starting from a tetrahedral structure with an out-of-plane CH_2 resulted in the square-planar structure, shown in Figure 1, where CH_2 is in plane. Keeping the optimized structural parameters of the planar complex **6a**, calculations have been performed with a tetrahedral deformation as shown.



Results shown in Table III indicate a stable planar structure. In order to test the reliability of the effective core potential, we have performed a calculation including 5s and 5p electrons explictly as valence electrons. Results in Table III also support the planar structure. We can say that in this complex a tetrahedral form[22] does not exist as a local minimum.

No structural data for an unsubstituted carbene complex of platinum are available.[23] In order to test the reliability

Table III. Relative Energy (in kcal/mol) of Tetrahedrally Deformed Carbene Complex 6a

	effective core potential	
θ deg	$4d^{10}5s^25p^6$ core	$4d^{10}$ core
90	0	0
78	1.9	3.4
66	5.6	7.0
55	12.6	14.9

[a] The optimized geometrical parameters for θ = 90° (**6a**) with the $4d^{10}5s^25p^6$ core are assumed except for the deformation angle θ.

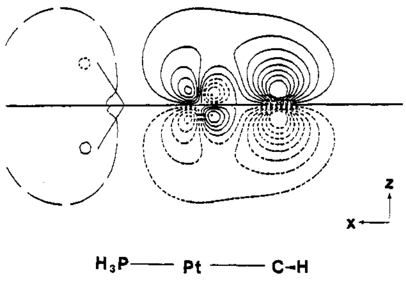
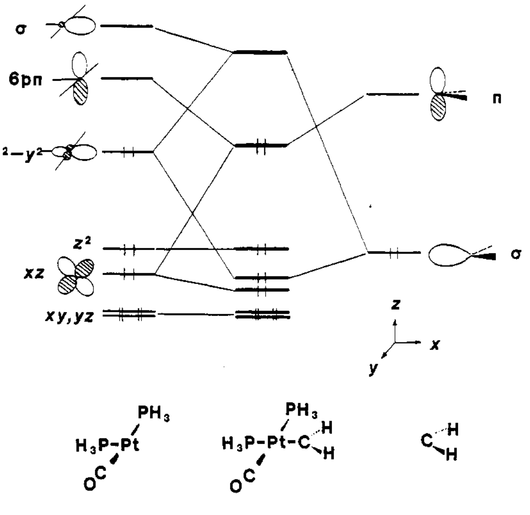


Figure 3. The projection of the HOMO of *cis*-$Pt(PH_3)_2(CH_2)(CO)$ (**4**). Solid and dotted lines represent positive and negative lobes, respectively, of the molecular orbital.

Scheme II



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of our structural prediction, we have carried out partial geometry optimizations for some experimentally established structures. In *cis*-Pt(PH$_3$)Cl$_2$CHNH$_2$ we found the planar structure to be preferred in agreement with the experiment for Pt(PPh$_3$)Cl$_2$CHNMe$_2$.[14] We found Pt(PH$_3$)$_3$(CO) to be tetrahedral, again in agreement with the experiment for Pt(PPh$_3$)$_3$(CO).[24] On the basis of these agreements, we believe that the square-planar carbene complex 4 is real.

The square-planar geometry of four-coordinate complexes is often associated with formal d^8 complexes. Indeed according to our result, the square-planar carbene complex 6 reveals a d^8-like character. The Mulliken populations shown in Table I clearly indicate that $d_{x^2-y^2}$ has a population of 1.171, very similar to that for *cis*-Pt(PH$_3$)(CHNH$_2$)Cl$_2$, a typical d^8 complex. The orbital correlation diagram, in Scheme II, shows that the bonding orbital consisting of the CH$_2$ π orbital and the Pt 6pπ orbital is lower in energy than the antibonding orbital CH$_2$ σ -Pt dσ and is the HOMO in the complex. The projection of this HOMO in the *xz* plane shows clearly, as shown in Figure 3, that the electron density of this orbital is substantially localized to the CH$_2$ π orbital, which interacts with the Pt 6pπ orbital bondingly and with the already occupied Pt d_{xz} orbital antibondingly. If the CH$_2$ group is perpendicular to the molecular plane, this attractive π-orbital interaction would be lost; in fact, the rotation of the planar CH$_2$ of 4 into the perpendicular position costs about 45 kcal/mol. The CH$_2$ π + Pt pπ interaction thus is the origin of the stability of this planar carbene intermediate.

In order to further assess the importance of this π conjugation, we have optimized both CH$_2$-coplanar **6a** and CH$_2$-perpendicular **6b** forms of *trans*-Pt(PH$_3$)$_2$(CH$_2$)(CO) under a C_{2v} constraint, as shown in Figure 1. An optimization without symmetry constraints starting from a tetrahedral structure also converged to **6a**, again excluding the possibility of a tetrahedral local minimum. The coplanar form is more stable by 47.0 kcal/mol at the MP2 level than the perpendicular form. A comparison of geometries in Figure 1 shows that both coplanar forms 4 and **6a** have substantially shorter Pt–C distances (1.881 and 1.911 Å, respectively) than the perpendicular form **6b** (2.028 Å), due to this π bonding. Though no structural data for unsubstituted carbene complexes of platinum are available, our results for the perpendicular form may be compared with experimental Pt–C distances in Pt(II) complexes,[23] for instance, 2.009 Å in Pt(Cl)$_2$(PEt$_3$)(C(NPhCH$_2$)$_2$),[23b] where carbene is perpendicular due to steric repulsion of bulky substituents.[10]

The present result is in clear contrast to Ni(CO)$_3$(CH$_2$), which was predicted to be tetrahedral by an ab initio calculation with a large basis set without the effective core potential.[26] This difference is probably attributable to the relativistic effect in Pt. As is well-known,[27] the relativistic effect stabilizes the p orbital of a heavy atom, favoring a strong pπ–dπ interaction.

V. Transition State between Ketene and Carbene Complexes

At the end of this study, we have determined the structure and characterized the transition state **5** connecting the ketene complex **3** and the carbene intermediate 4. The optimized transition-state geometry **5**, shown in Figure 1, has no symmetry and is a late transition state, resembling the product carbene complex. The transition state is asynchronous in the sense that the CC bond has been nearly completely broken whereas the CH$_2$ group is in the middle of rotation, with a CPtCH dihedral angle of 38°. The direction of the approximate reaction coordinate at the transition state, i.e. the normal coordinate with the only imaginary frequency, shown by arrows in Figure 1, is mainly the CH$_2$ rotation supplemented with CPtC bending.

As shown also in Figure 1, the barrier height from the ketene complex is calculated to be about 37 kcal/mol at the more reliable MP2 level. Though this value agrees with the latest experimental activation energy of 34 kcal/mol for the thermolysis of Pt(PPh$_3$)$_2$(CH$_2$=C=O) in the solid state,[5c] it seems to be too high compared with the calculated activation energy of 19 kcal/mol for CH$_2$=C=O dissociation from Pt(PH$_3$)$_2$(CH$_2$=C=O) (**3**). Experiments by Miyashita[5c] show that the thermolysis of Pt(PPh$_3$)$_2$(CD$_2$=C=O) in solution in the presence of free CH$_2$=C=O gives no significant quantity of CD$_2$=CH$_2$, eliminating the possibility of C—C fission through coupling with free ketene. Though we do not know the origin of this discrepancy, there is a possibility of dimerization between two carbene complexes or between a carbene complex and a ketene complex, lowering the effective barrier for the CH$_2$ + CH$_2$ coupling.[25] For a complete resolution of the reaction mechanism, alternative paths such as possibilities of a three-coordinate intermediate and direct coupling of two ketene complexes would have to be examined.

VI. Conclusions

Ab initio MO studies on the structure and energetics of ketene and carbene carbonyl complexes of Pt(PH$_3$)$_2$ led to the following results.

(1) The most stable ketene complex has the η^2(C–C) square-planar structure **3** with the CH$_2$ group perpendicular to the molecular plane and is d^8-like. The η^2(C–O) square-planar structure with the CH$_2$ group in the molecular plane is a local minimum, less stable by about 7 kcal/mol. A tetrahedral complex does not exist. The CH$_2$=C=O binding energy and the dissociation barrier height in **3** are calculated to be 13 and 19 kcal/mol, respectively.

(2) The carbene carbonyl complex 4 derivable from **3** is cis square planar and is about 28 kcal/mol above **3**. The CH$_2$ group is within the plane of the molecule, and the strong CH$_2$ $\pi \rightarrow$ Pt pπ interaction is the origin of its stability. A tetrahedral complex or a cis square-planar complex with perpendicular CH$_2$ is not a local minimum.

(3) The transition state from **3** to 4 is a late transition state resembling the product 4 and is asynchronous in the sense that the CC bond has been completely broken whereas the CH$_2$ group is still in the midst of rotation. The barrier height of 37 kcal/mol seems to be too high for

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efficient carbene complex formation and subsequent CH_2–CH_2 coupling.

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Low-Valent Cyanocobaltate Chemistry. 3. Reactions of $[(\eta^5\text{-}C_5H_5)Co(CN)(CO)]^-$ with Electrophiles, Nucleophiles, and Redox Agents. Synthesis of New (η^5-Cyclopentadienyl)cobalt Cyanide Complexes[1]

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Details of the syntheses and reactivity of (K-crown)[Cp(CN)(CO)] (**1a**) (crown = 18-crown-6 ether), PPN[Cp(CN)(CO)] (**1b**), (K-crown)[CpCo(CN)PPh_3] (4), and (K-crown)[CpCo$(CN)_2$] (**10a**) are presented. Compound **1a** is readily formed by reaction of CpCo$(CO)_2$ with cyanide in aprotic media. Reaction of CpCo$(CO)_2$ with excess cyanide under forcing conditions results in the dissociation of cyclopentadienide anion instead of $[CpCo(CN)_2]^{2-}$ formation. Although the $[CpCo(CN)_2]^{2-}$ anion appears to be extremely basic and reactive, an impure form can be isolated by the low-temperature reduction of **10a** in DMF. The electrophiles acetyl chloride, benzyl bromide, and methyl fluorosulfate do not react with **1a** to form isocyanides but unexpectedly produce CpCo$(CO)_2$ and a variety of Co(II) and Co(III) compounds. The pathways that culminate in these products are suggested to originate from an initial one-electron transfer yielding the intermediate [Cp(CN)(CO)]. Treatment of **1a** or **1b** with tosyl chloride yields $[CpCo(CN)_2(\eta^1\text{-}SO_2C_6H_4CH_3)]^-$ and cyanide-bridged cyclopentadienylcobalt(III) polymers, while **1a** or **1b** reacts cleanly with R_3SnCl reagents to form the expected isocyanide complexes. $Hg(CN)_2$ oxidizes **1** to $CpCo(CN)_3^-$. Acyl chlorides lacking α-hydrogens react with **1** to produce novel bis(acyl isocyanide) complexes CpCo$(CNCOR)_2$ in low yields. The spectroscopic characterization of these compounds is presented, and the nature of the cyanide ligand's influence on low-valent metal centers is discussed.

Introduction

We have communicated the crown ether assisted synthesis of the $[CpCo(CN)(CO)]^-$ anion (1; Cp = η^5-C_5H_5) and preliminary observations concerning its reactivity.[1a] Of special interest to us was the opportunity to characterize the properties of cyanide as a ligand in the environment of a relatively electron-rich, low formal oxidation state metal. This could be done by comparing the chemical and physical properties of 1 with those of the well-known compounds CpCoL_2 (L = CO, phosphines, or isocyanides). CpCo$(CO)_2$ has been an important molecule in the recent development of transition-metal organometallic chemistry, providing entries into metal clusters,[3] C–C bond formation studies,[4] new organic synthesis methods,[5] and complexes of novel ligands.[6] CpCo$(CO)_2$ is considered to be a relatively electron-rich metal carbonyl,[7] and this can be regarded as a consequence of the CpML_2 geometry.[8] The availability of the even more basic CpCo$(PR_3)_2$ complexes has thus provided a test bed for understanding the chemical consequences of extremely electron-rich metal centers.[9] We anticipated that spectroscopic and chemical reactivity comparisons between these compounds and 1 would provide insight into the relative donor and acceptor properties of the cyanide ligand in an environment where we assumed its π-acceptor abilities would be important.

In our preliminary study,[1a] we observed that the CN ligand in 1 is labile; thus reactions of 1, which are dissociative in nature, such as reactions with alkynes, should be little different from the corresponding reactions of CpCo$(CO)_2$, as we observed. On the other hand, reactivity dependent on metal-centered basicity or electron density should provide a significant contrast between 1 and CpCo$(CO)_2$ (2), especially if the σ-donor properties of the CN ligand were dominant. This distinction was observed in the respective reactions of 1 and 2 with HgX_2, X = Cl or CN, and in the resistance of 1 to reduction. This data suggested that the donor strength of CN is the dominant property of this ligand in 1.

If 1 is as electron-rich as it appears from the above results, then analogues of 2 such as CpCo(CO)PPh_3 (**3a**) and CpCo$(PMe_3)_2$ (**3b**) should be better models for its chemical behavior. Compounds 3 are characterized by their much greater basicity and nucleophilicity relative to 2. We thus began an investigation of the reactions of 1 with electrophiles. In our previous report, we noted that reactions of 1 with simple alkyl and acyl halides were complex but that in the case of acyl halides lacking α-

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