Organometallic Chemistry

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Synthesis and Reactivity of a Cationic Platinum(II) Alkylidene Complex**

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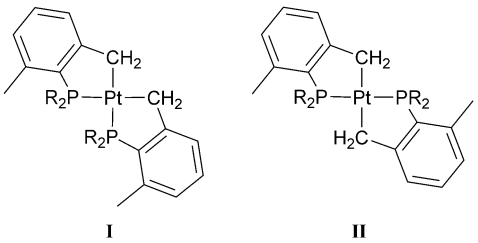
The last decades have witnessed an explosive growth of interest in the chemistry of transition-metal carbenes,[1,2] which has mainly been due to their important catalytic applications. A great deal of effort has converged in recent years on platinum- and gold-catalyzed reactions[3] that occur with participation of carbene species as active reaction intermediates.[3–5] For these systems Fürstner and co-workers have established an analogy between metal carbenes and metal-stabilized carbocationic structures and proposed the term carbenoid to illustrate this ambiguity.[3a,b,4]

For the Group 10 elements, carbene complexes with carbocyclic-,[6] N-heterocyclic-,[7] and heteroatom-stabilized-carbene[8] ligands are known.[9] However, related complexes that contain {M=C(R)(R′)} units, where R and R' are hydrogen or hydrocarbyl groups are very rare. The first such nickel complex was reported by Mindiola and Hillhouse in 2002 and contains a Ni^0 center bound to a $C(Ph)_2$ carbene fragment.[10] Interestingly, only a year later, a cationic Pd^{II} derivative of a non-heteroatom-stabilized carbene ligand $C(p\text{-tolyl})_2$ was prepared and structurally characterized by X-ray crystallography.[11] The latter complex features a rather long $Pd{-}C_{carbene}$ bond (1.976 Å), which is indicative of only a minor stabilization of the carbene σ donor by back-bonding from filled palladium dπ orbitals.

In view of the importance of cationic platinum(II) alkylidene species, $[Pt^{II}{=}C(R)(R')]^+$, in catalysis[3,5] we planned to generate and characterize some compounds of this kind. Over the years, we have succeeded in ascertaining the structural properties of related cationic Ir^{III} alkylidenes.[12] Studies of the energetics of $\{Pt{=}CH_2\}^+$ by ab initio calculations revealed a high bond energy that is largely due to relativistic effects.[13] On the assumption that the bonding for a cationic $\{Pt^{II}{=}C(R)(R')\}^+$ unit follows the dative model,[14] and taking into account that similar to Pd^{II}[11] little back-donation from the cationic platinum(II) center to the alkylidene can be expected,[15] it is reasonable to think that failure to isolate such species is most probably due to their high reactivity rather than to intrinsic weakness of the platinum–alkylidene bond. Indeed, Menjón, Forniés, and co-workers have demonstrated recently that, contrary to isolable $[M]{=}CF_2$ derivatives of Group 8 and 9 metals, the analogous $[Pt]{=}CF_2$ units are highly reactive and need extra stabilization by formation of a chelating pyridinium ylide structure.[16]

We envisaged that sterically protected platinum bis(metallacycles)[17] containing five-membered rings as a result of metalation of aryl phosphine ligands (structures **I** and **II** in Scheme 1) could be suitable candidates for this enterprise, as cationic benzylidene structures could then be readily generated by α-hydride abstraction.[18] Related platinum metallacycles have already been reported.[19a,20] With the express intention of hindering C–C coupling between the benzylidene and benzyl termini of the desired cationic alkylidene formulations, a *trans* geometry like **II** in Scheme 1 was chosen. Reaction of $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene) with the bulky xylyl phosphine[19,21] $PiPr_2Xyl$ (Xyl = 2,6-$Me_2C_6H_3$) under the conditions of Scheme 2 yielded the desired *trans* bis(metallacycle) **1** as a colorless microcrystalline solid, in yields of isolated product of close to 80%. Complex **1** was fully characterized by microanalysis and NMR spectroscopy (see the Supporting Information).



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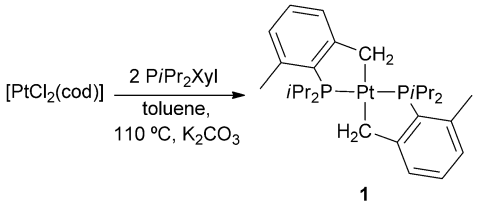
Scheme 1. *cis*- and *trans*-Bis(platinacycle) structures derived from benzylic metalation of aryl phosphine ligands.



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Scheme 2. Synthesis of the *trans*-bis(platinacycle) **1**.

Upon dissolving an equimolar solid mixture of complex **1** and $Ph_3C^+PF_6^-$ in CH_2Cl_2 at −80 °C, a dark green, almost black solution was obtained. Warming to higher temperatures

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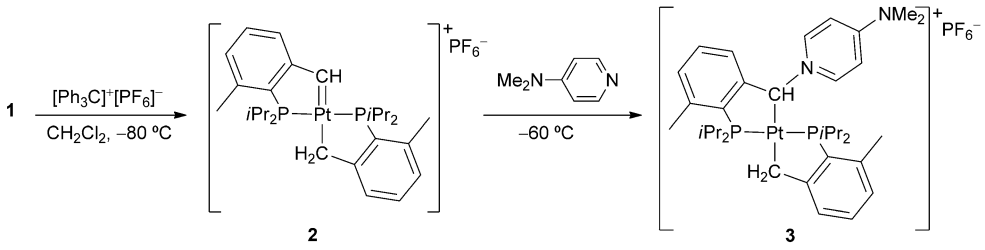
(ca. −30 °C) caused no additional changes, and upon removal of the solvent at −30 °C, a dark green oily material was obtained. Owing to its very high reactivity toward oxygen and moisture and its relatively poor thermal stability (see below), microanalytically pure samples of **2** could not be procured. Nevertheless, NMR data and reactivity studies summarized in Scheme 3 and 4 demonstrate beyond any doubt the proposed formulation. Cationic metal complexes that feature alkyl and alkylidene ligands are very reactive species, intrinsically difficult to detect. They are proposed intermediates for some catalytic processes, such as C1 polymerization of diazocompounds[22a] and Fischer–Tropsch synthesis of long-chain hydrocarbons.[22b] The comparatively higher stability of **2** (discussed below) no doubt arises from the *trans* arrangement of its benzylidene and benzyl units.[23]



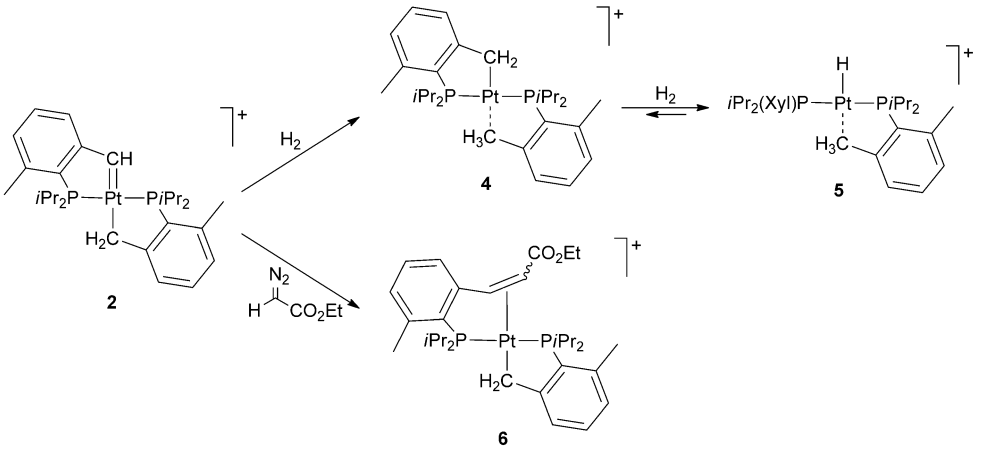
Scheme 3. Generation of alkylidene **2** and its stabilization as a pyridinium ylide.

In accord with the proposed structure, two widely separated signals are recorded in the ^{1}H NMR spectrum (0 °C) for Pt=C*H* (δ 15.61 ppm, 1H; dd, $^3J_{HP} = 4.1$ Hz and $^3J_{HP'} = 8.2$ Hz, $^2J_{HPt} = 46.6$ Hz, respectively) and Pt–CH_2 protons (5.16 ppm, 2H; broad singlet, $^2J_{HPt} = 48.2$ Hz). Corresponding ^{13}C NMR signals (at 0 °C) feature, once more, distinct chemical shifts at δ 209 ($^1J_{CH} = 137$ Hz, $^1J_{CPt} = 740$ Hz) and 29.7 ppm ($^1J_{CH} = 131$ Hz, $^1J_{CPt} = 365$ Hz). In the ^{31}P{^{1}H} NMR spectrum obtained at the same temperature, the two phosphorous atoms give rise to an AB pattern ($\delta_A = 76.0$ ppm, $\delta_B = 77.3$ ppm, and $^2J_{AB} = 351$ Hz), which is consistent with their *trans* distribution ($^1J_{PPt}$ coupling have values of 2480 and 2605 Hz, respectively). As already mentioned, complex **2** exhibits only moderate thermal stability and degrades at room temperature to a mixture of unidentified products. ^{31}P{^{1}H} NMR monitoring discloses first-order dependence in the concentration of **2** and a half-life of about 44 h at 25 °C ($\Delta G^{\neq} = 24.7 \pm 0.4$ kcal mol^{-1}; Supporting Information, Figure S1).

Further characterization of the alkylidene structure of **2** was achieved by chemical studies. Low-temperature addition of Lewis bases (PMe_3, pyridine, or dmap (4-dimethylaminopyridine)) to solutions of **2** provided the corresponding ylidic complexes, of which only the dmap derivative **3** is shown in Scheme 3 and will be discussed here. A dramatic shift of the alkylidene proton of **2** is observed upon ylide formation (from 15.61 to 5.99 ppm; $^2J_{HPt} = 49$ Hz, $^1J_{CH} = 137$ Hz), whereas ^{31}P{^{1}H} NMR data corroborate that the *trans* arrangement of the two metallacycles is maintained. The molecular structure of **3** was unequivocally confirmed by X-ray studies (Supporting Information, Figure S2).

Compound **2** reacted also with H_2 (1 bar; −30 °C to room temperature) to yield the anticipated cationic cyclometalated platinum(II) complex **4** (Scheme 4) that is stabilized by an agostic interaction,[21a] along with the also agostic hydride **5** (ca. 1:3 ratio)[24] and some minor unidentified products. Removal of volatile substances provided exclusively **4**, which was independently generated (see the Supporting Information) by protonation of the neutral complex **1** with $HBAr_F$ ($BAr_F = B[3,5\text{-}C_6H_3(CF_3)_2]_4$). Previous work by Baratta, Stoccoro, and co-workers resulted in the formation of the PPh_2Xyl and PCy_2Xyl analogues of **4** from the reaction of the neutral *trans*-$[Pt(CH_3)Cl(PR_2Xyl)_2]$ derivatives with $NaBAr_F$ (hydrido species similar to **5** were also described).[21a] The T-shaped structures proposed for **4** and **5** in Scheme 4 are secured by pertinent analogies between their ^{1}H, ^{13}C, and ^{31}P NMR data and those already described for the above-mentioned compounds.[21a] 2D EXSY studies of **4** between 25 and 60 °C indicate no exchange of the methylene and methyl groups of the two aryl rings. However, exchange of the methyl groups of the agostic xylyl ring occurs at 20 °C. An X-ray study of **4**, to be reported in due course, confirmed the existence of an agostic interaction characterized by a Pt···CH_3 distance of about 2.32 Å.

As a final test for the alkylidene structure of **2**, its reaction with the diazocarbene compound, $N_2C(H)CO_2Et$ (EDA), was tested. As shown in Scheme 4, a mixture of *cis* and *trans*



Scheme 4. Reactions of cationic complex **2** with H_2 and EDA (ethyl diazoacetate).

isomers of a terminal alkene complex **6**, resulting from C–C coupling between EDA and **2**, was formed.[25] The two compounds were separated by fractional crystallization and characterized by spectroscopy and X-ray studies (Figure 1).[26] Despite the presence of two distinct reactive sites in **2**, namely the {Pt–CH_2} and the {Pt=CH} moieties, the high electrophilicity of the latter is expected to override the reactivity of the alkyl terminus. Hence, *cis*- and *trans*-**6** could result from direct cross-coupling of the two carbene fragments. Notice, however, that a somewhat more elaborated reaction pathway, consisting of migratory insertion of the alkyl unit of **2** into a transient, EDA-derived coordinated carbene, followed by β-hydrogen elimination and a 1,2-H shift from platinum to the benzylidene carbon, could also explain the formation of complexes **6**. Nevertheless, this alternative route appears unlikely, because performing the reaction of **2** with EDA in the presence of 1 equiv of pyridine inhibits completely formation of **6**, owing to quenching of the alkylidene electrophilicity by ylide formation (see above).

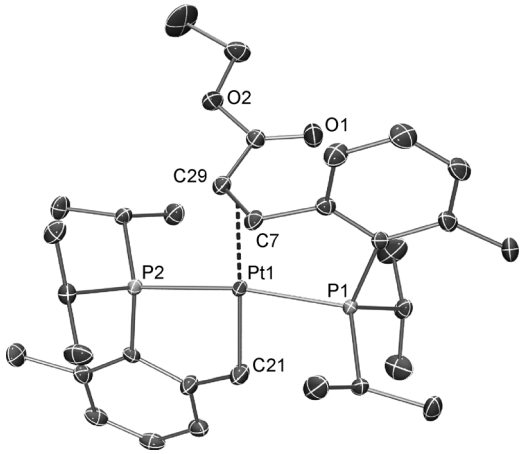


Figure 1. ORTEP view of *cis*-**6** with ellipsoids set at 30% probability (PF_6^- and hydrogen atoms omitted for clarity). Selected bond lengths [Å]: Pt1–P1 2.3288(8), Pt1–P2 2.330(1), Pt1–C21 2.056(4), Pt1–C7 2.225(4), Pt1–C29 2.248(3).

In summary, a highly electrophilic cationic platinum(II)–alkylidene complex **2** has been generated and shown to feature moderate thermal stability and enhanced chemical reactivity toward nucleophiles.

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[26] See the Supporting Information for further details of the characterization by spectroscopy and X-ray diffraction studies of **3**, cis-**6**, and trans-**6**.

