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Correlations and Contrasts in Homo- and Heteroleptic Cyclic (Alkyl)(amino)carbene-Containing Pt^0 Complexes

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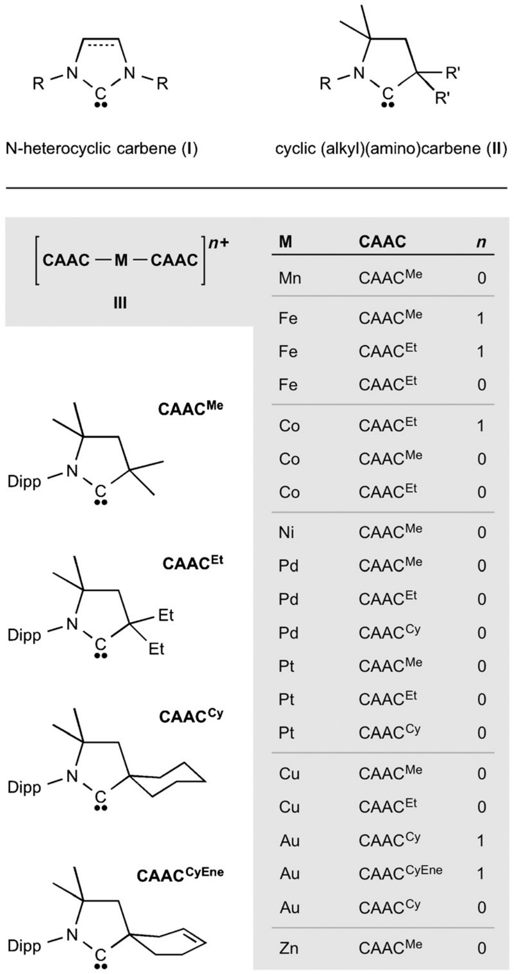
Abstract: An improved synthetic route to homoleptic complex $[Pt(CAAC^{Me})_2]$ (CAAC = cyclic (alkyl)(amino)carbenes) and convenient routes to new heteroleptic complexes of the form $[Pt(CAAC^{Me})(PR_3)]$ are presented. Although the homoleptic complex was found to be inert to many reagents, oxidative addition and metal-only Lewis pair (MOLP) formation was observed from one of the heteroleptic complexes. The spectroscopic, structural, and electrochemical properties of the zero-valent complexes were explored in concert with density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. The homoleptic $[Pt(CAAC)_2]$ and heteroleptic $[Pt(CAAC)(PR_3)]$ complexes were found to be similar in their spectroscopic and structural properties, but their electrochemical behavior and reactivity differ greatly. The unusually strong color of the CAAC-containing Pt^0 complexes was investigated by TD-DFT calculations and attributed to excitations into the LUMOs of the complexes, which are predominantly composed of bonding π interactions between Pt and the CAAC carbon atoms.

Introduction

The isolation of stable singlet carbenes, credited to the groups of Bertrand and Arduengo, has dramatically broadened the range of strongly donating ligands available to researchers, and has led to stunning advances in inorganic, organometallic, and main-group chemistry, as well as the fields of homogeneous and organocatalysis.[1] The field of stable carbenes is perhaps best represented by their most known sub-class, the so-called N-heterocyclic carbenes (NHCs, **I**; Figure 1). However, many other types exist. Of these, cyclic (alkyl)(amino)carbenes (CAACs, **II**), a type of stable carbene pioneered by the group of Bertrand a decade ago, are arguably the class currently experiencing the most rapid growth in interest.[2]

Although the utility of NHCs is based mostly on their strong, consistent, and usually predictable electron-donating ability, CAACs have found a fascinating niche as donors that can adapt their bonding to suit their environment. This bonding can lie anywhere on the continuum from pure donor to full multiple (quinoidal) bonding, depending on the extent of π acceptance by the carbene carbon's empty p orbital. This adaptability has been exploited very recently in the synthesis of complexes of the form $[M(CAAC)_2]^{n+}$ (M = Group 7–12 metals; **III**;



M	CAAC	n
Mn	$CAAC^{Me}$	0
Fe	$CAAC^{Me}$	1
Fe	$CAAC^{Et}$	1
Fe	$CAAC^{Et}$	0
Co	$CAAC^{Et}$	1
Co	$CAAC^{Me}$	0
Co	$CAAC^{Et}$	0
Ni	$CAAC^{Me}$	0
Pd	$CAAC^{Me}$	0
Pd	$CAAC^{Et}$	0
Pd	$CAAC^{Cy}$	0
Pt	$CAAC^{Me}$	0
Pt	$CAAC^{Et}$	0
Pt	$CAAC^{Cy}$	0
Cu	$CAAC^{Me}$	0
Cu	$CAAC^{Et}$	0
Au	$CAAC^{Cy}$	1
Au	$CAAC^{CyEne}$	1
Au	$CAAC^{Cy}$	0
Zn	$CAAC^{Me}$	0

Figure 1. Top: Generalized NHC and CAAC bases. Bottom: Isolated homoleptic transition-metal complexes of the form $[M(CAAC)_2]^{n+}$.

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Figure 1) by a number of groups working both separately and collaboratively, those of Bertrand, Roesky, Frenking, Dittrich, Kaim, Parameswaran, Neidig, Deng, Meyer, Ungur, Stalke, Dalal, Peters, and Ackermann.[3–8] The sheer quantity of work on complexes of the form $[M(CAAC)_2]^{n+}$ published since the beginning of 2013 (to say nothing of the equally unusual chemistry of main-group CAAC adducts[2f]) is astounding and reflective of the unique abilities of these ligands.

In these studies, CAAC ligands have allowed the surprising synthesis of complexes, which at first glance contain transition metals with uncommon oxidation states (e.g., Cu^0, Ag^0, Au^0). These feats can largely be attributed to two key properties of the $[M(CAAC)_2]^{n+}$ motif: 1) the bulky CAAC ligands have the necessary steric bulk to protect reactive metal centers; and 2) the two relatively low-energy empty carbon-based π orbitals, which together can accept one or two residual electrons from high-energy orbitals on the central metal. In other words, otherwise unfavorable metal electron configurations can be stabilized by taking advantage of the ability of CAAC ligands' π orbitals to act as electron sinks.

Although the unusual electronic structures of these $[M(CAAC)_2]^{n+}$ complexes are grounds enough to warrant further exploration, their reactivity should not be overlooked. These complexes have already shown, for example, electrochemical and catalytic activity, and the ability to activate small molecules, such as dihydrogen and carbon dioxide.[3–8] Our entry into this field was motivated by a desire to prepare alternatives to the very useful and strongly Lewis basic complexes $[Pt(PR_3)_2]$ (R = Et, *i*Pr, Cy) for various purposes, such as catalytic dehydrocoupling,[9] oxidative addition of E–X bonds,[10] and the formation of metal-only Lewis pairs (MOLPs).[10e,11] Herein, we describe the synthesis of both homoleptic $[Pt(CAAC)_2]$ and heteroleptic zero-valent complexes of platinum and their reactivity towards Lewis acidic main-group compounds.

Results and Discussion

Synthesis of CAAC-containing Pt^0 complexes

During the production of this manuscript, the groups of Stalke, Frenking, and Roesky presented the synthesis of six homoleptic Pd^0 and Pt^0 CAAC complexes by the treatment of $[M(PPh_3)_4]$ (M = Pd, Pt) with three different CAAC ligands (Figure 1).[6c] Recently, we developed a synthesis of one of these complexes, $[Pt(CAAC^{Me})_2]$ (**1**, Figure 2), by using the convenient triolefin Pt^0 complex $[Pt(nbe)_3]$ (nbe = norbornene). The synthesis requires no heating or fractional crystallization, because the nbe ligands and solvent pentane can be removed under vacuum. This produced an orange solid, without the co-crystallized THF molecule reported in the published procedure, in 96% yield, significantly higher than the published result.[6c] The recently published synthesis of **1** also involves the liberation of four molar equivalents of triphenylphosphine. Our synthesis thus represents a marked improvement in atom efficiency and simplicity.

The NMR spectroscopic data of our material was found to be essentially the same as the published data. Single crystals of $\mathbf{1}\cdot C_6H_6$ suitable for a diffraction study were grown from benzene, and showed statistically insignificant Pt–C bond-length variation from the published molecular structure of $\mathbf{1}\cdot 0.5\,THF$ ($\mathbf{1}\cdot C_6H_6$: 1.965(2), 1.969(2) Å; $\mathbf{1}\cdot 0.5\,THF$: C–Pt 1.964(5), 1.967(5) Å). The CAAC ligands in both structures were found to coordinate in an approximately linear fashion across the Pt center (C-Pt-C angle: $\mathbf{1}\cdot C_6H_6$: 171.13(7)°; $\mathbf{1}\cdot 0.5\,THF$: 170.9(2)°). However, the two structures differ markedly in their degree of alignment of the CAAC ligands, with the NCC planes in our structure of $\mathbf{1}\cdot C_6H_6$ being oriented nearly orthogonally (N-C-C-N torsion: 73.1°), but those of $\mathbf{1}\cdot 0.5\,THF$ being between *syn* and *anti*-arrangements (N-C-C-N torsion: 48.7°). If we consider the angle between the two least-squares planes of the CAAC ligands, the differences are likewise very large ($\mathbf{1}\cdot C_6H_6$ 70.0°; $\mathbf{1}\cdot 0.5\,THF$ 30.3°). The alignment of the CAAC ligands in $\mathbf{1}\cdot 0.5\,THF$ was discussed by Stalke, Frenking, and Roesky[6c] and attributed to the stronger π backdonation of the CAAC ligands.[2e] That our structure shows a very different degree of alignment, but apparently equivalent Pt–C distances, suggests instead that the alignment has little bearing on the ability of the Pt center to undergo π backbonding with the ligands, and is perhaps not as diagnostic as the authors of that paper[6c] suggest.

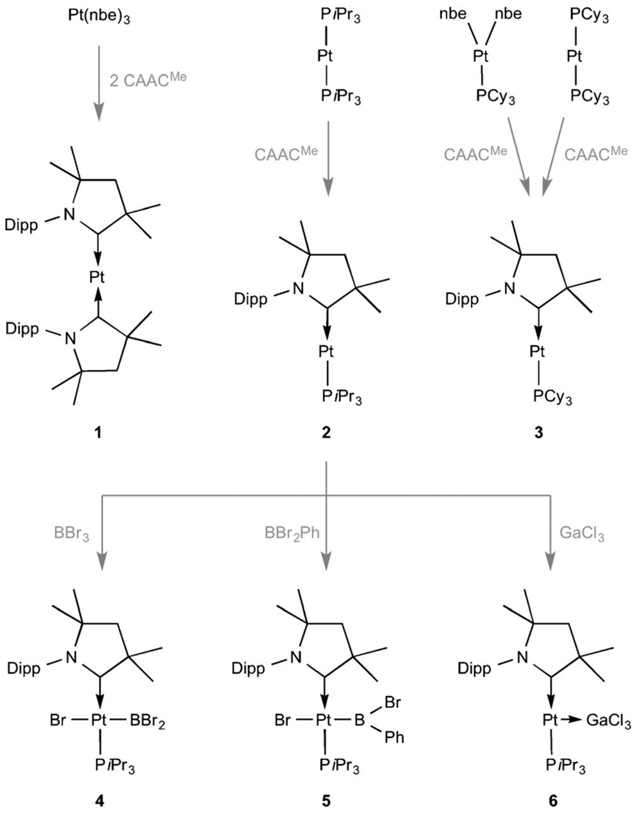

Figure 2. Synthesis of homo- and heteroleptic CAAC complexes of Pt^0, and reactivity of heteroleptic complex **2a**.

Complex **1** was prepared in an attempt to create a superior transition-metal Lewis base to bis(phosphine) Pt^0 complexes frequently used in our laboratories. However, despite its presumably higher electron density, **1** was found to be inert towards a range of haloborane Lewis acids including BBr_2Ph,

BBr_2Fc (Fc = ferrocenyl), BBr_2Dur (Dur = 2,3,5,6-tetramethylphenyl), $B_2Br_2(NMe_2)_2$ and $B_2Cl_2Dur_2$, even at elevated temperatures (up to 60 °C). When **1** was treated with BH_2Dur, BH_2Mes, or $GaCl_3$, slow and unselective reaction of the starting materials was observed from which we were unable to isolate or identify any products. With BBr_3, complex **1** decomposes to form a complex mixture from which we were able to isolate only the imidazolium salt $[CAAC^{Me}H][BBr_4]$. The high steric bulk of **1** presumably precludes its metal-centered Lewis basicity, and over time, allows slower ligand-cleavage reactions to predominate (Figure 3).

Given these results, we sought a compromise that combined the metal accessibility of bis(phosphine) complexes $[Pt(PR_3)_2]$ (R = Et, *i*Pr, Cy) with the presumed higher electron density of $[Pt(CAAC)_2]$ complexes. The clearest choice was the monophosphine, mono(CAAC) scaffold $[Pt(CAAC)(PR_3)]$. In 2010, we developed a synthetic route to related monophosphine, mono(NHC) complexes of Pd^0 and Pt^0 by the simple replacement of one phosphine ligand of $[M(PR_3)_2]$ with the carbene.[12] This strategy was hereby extended to CAAC ligands by using the Pt^0 complexes $[Pt(PR_3)_2]$ (R = *i*Pr, Cy), resulting in the heteroleptic complexes $[Pt(CAAC^{Me})(PR_3)]$ (R = *i*Pr, **2**; R = Cy, **3**; Figure 2). The complexes each showed single ^{31}P resonances with ^{195}Pt satellites (**2**: $\delta = 69.4$ ppm, $^1J_{PPt} = 3148$; **3**: $\delta = 57.7$ ppm, $^1J_{PPt} = 3110$), similar to those found for related heteroleptic complexes $[Pt(NHC)(PCy_3)]$ (NHC = I*t*Bu = $:CN_2(tBu)_2C_2H_2$ $\delta = 59.7$ ppm, $^1J_{PPt} = 3986$; NHC = IMes = $:CN_2(Mes)_2C_2H_2$ $\delta = 58.4$ ppm, $^1J_{PPt} = 3640$), but with significantly smaller ^{31}P–^{195}Pt coupling constants.[12] Single-crystal X-ray crystallographic studies of **2** and **3** showed considerably shorter Pt–C^{carbene} distances (**2**: 1.973(3); **3**: 1.86(3) Å) than the NHC analogues $[Pt(NHC)(PCy_3)]$ (NHC = I*t*Bu: 2.027(3); NHC = IMes: 1.991(2) Å), but longer Pt–P distances in the CAAC complexes (**2**: 2.2393(7); **3**: 2.239(1) Å) than the NHC complexes (I*t*Bu: 2.211(1); IMes: 2.228(1) Å). These effects are presumably due to the superior σ donation and π-accepting properties of the CAAC ligands. However, it should be noted that disorder of the CAAC ligand of **3** over two orientations limits the accuracy of the distances in this structure.

The monophosphine $[Pt(nbe)_2(PCy_3)]$, prepared by addition of tricyclohexylphosphine to $[Pt(nbe)_3]$ (see the Supporting Information for synthesis, characterization and single-crystal X-ray structure), was also found to be a convenient precursor to **3**, giving the complex in slightly higher yield (72 %) than the route using $[Pt(PCy_3)_2]$.

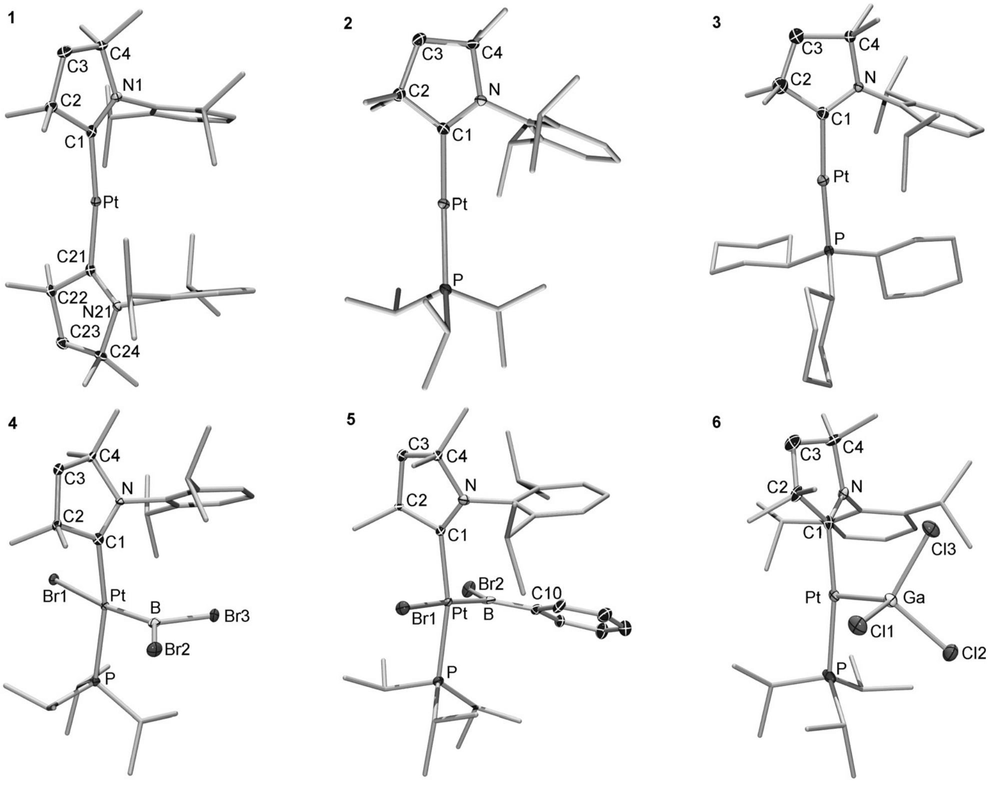

Figure 3. Crystallographically derived molecular structures of **1**–**6**. Thermal ellipsoids drawn at the 50 % probability level. Solvent molecules (one molecule of benzene for **1**, one molecule of toluene for **5**), and some ellipsoids have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **1**: Pt–C1 1.965(2), Pt–C21 1.969(2), N1–C1 1.329(2), N2–C21 1.326(2); C1-Pt-C21 171.13(7). For **2**: Pt–C1 1.973(3), Pt–P 2.2393(7), N–C1 1.320(3); C1-Pt-P 172.55(7). For **3**: Pt–C1 1.86(3), Pt–P 2.239(1), N1–C1 1.25(4); C1-Pt-P 173.8(10). For **4**: Pt–B 1.960(4), Pt–C1 2.049(3), Pt–P 2.3491(8), Pt–Br1 2.5968(3), C1–N 1.306(4); C1-Pt-P 166.12(9), B-Pt-Br1 170.1(1). For **5**: Pt–B 1.986(4), Pt–C1 2.038(4), Pt–P 2.340(1), Pt–Br1 2.6190(4), C1–N 1.309(5); C1-Pt-P 166.4(1), B-Pt-Br1 169.80(14). For **6**: Pt–Ga1 2.3962(3), Pt–C1 2.021(3), Pt–P 2.3227(7), N–C1 1.323(4); C1-Pt-P 169.83(7), C1-Pt-Ga 91.32(7), P-Pt-Ga 98.44(2).

Reactivity of CAAC-containing Pt^0 complexes

Unlike complex **1**, the heteroleptic complex **2** was found to undergo much more facile reactivity. Treatment of **2** with either tribromoborane or dibromophenylborane (the latter with heating to 60 °C) led to the square-planar Pt^{II} boryl complexes **4** and **5**, products of oxidative addition of one B–Br bond to the metal center. The ^{31}P NMR signals of the products were found to be significantly shifted to lower frequencies from those of their precursor **2**, with drastically reduced coupling constants (**4**: $\delta = 22.1$ ppm, $^1J_{PPt} = 2397$; **5**: $\delta = 21.7$ ppm, $^1J_{PPt} = 2415$). Broad singlet ^{11}B NMR resonances were also detected for the complexes (**4**: $\delta = 54.0$ ppm; **5**: $\delta = 73.6$ ppm), effectively identical to those of their most comparable published complexes, the bis(phosphine) Pt^{II} boryl complexes *trans*-$[PtBr(BBr_2)(PCy_3)_2]$ ($\delta = 54$ ppm) and *trans*-$[PtBr\{BBr(o\text{-}Tol)\}(PCy_3)_2]$ ($\delta = 73$ ppm),[13] suggesting that the CAAC ligand has little electronic effect on the boryl ligand itself.

Likewise, the Pt–B distances of **4** and **5** (**4**: 1.960(4); **5**: 1.986(4) Å) are identical to those of their corresponding bis(phosphine) counterparts *trans*-[PtBr(BBr$_2$)(PCy$_3$)$_2$] (1.963(6) Å) and *trans*-[PtBr{BBr(*o*-Tol)}(PCy$_3$)$_2$] (1.982(3) Å) within experimental uncertainty. However, two points of distinction in the boryl–CAAC derivatives **4** and **5** are their significantly bent C-Pt-P angles (**4**: 166.12(9); **5**: 166.4(1)°) and somewhat distorted, non-planar CAAC heterocycles. Given their apparent electronic similarities to comparable bis(phosphine) derivatives, these distortions are most likely due to increased steric congestion around the metal from the bulky CAAC ligand.

In contrast to its oxidative addition reactions with bromoboranes, treatment of **2** with GaCl$_3$ gave instead the orange metal-only Lewis pair [(P*i*Pr$_3$)(CAAC^{Me})Pt→GaCl$_3$] (**6**), which showed a ^{31}P NMR resonance ($\delta = 53.1$ ppm, $^1J_{PPt} = 2425$) close to that of its bis(phosphine) congener [(Cy$_3$P)$_2$Pt→GaCl$_3$] ($\delta = 49.3$ ppm, $^1J_{PPt} = 2798$).[14] Single-crystal X-ray crystallographic study of **6** indicated that the complex has a shorter Pt–Ga distance (2.3962(3) Å) than that of [(Cy$_3$P)$_2$Pt→GaCl$_3$] (2.4019(2) Å) by a statistically significant but negligible amount (ca. 0.2 %). In addition, the GaCl$_3$ unit of **6** (Σ(∢Cl-Ga-Cl): 309.4°) is slightly more pyramidalized than that of [(Cy$_3$P)$_2$Pt→GaCl$_3$] (Σ(∢Cl-Ga-Cl): 314.3°). Overall, the spectroscopic and structural features of **6** suggest that the Lewis base strength of [Pt(CAAC^{Me})(P*i*Pr$_3$)] (**2**) is equivalent to or marginally greater than that of [Pt(PCy$_3$)], and, by extension, slightly weaker than [Pt(NHC)(PCy$_3$)] complexes as was determined in an earlier study.[12]

Electrochemical measurements

Cyclic voltammetry measurements were performed on the three Pt^0 complexes prepared herein (**1**–**3**), in addition to [Pt(PCy$_3$)$_2$] and [Pt(P*i*Pr$_3$)$_2$] for comparison (see the Supporting Information for further details). For complex **1**, we observed similar behavior to that reported by Stalke, Frenking, Roesky and co-workers, that is, a quasi-reversible oxidation wave in THF (our work: $E_{1/2} = -0.30$ V vs. [Cp$_2$Fe]/[Cp$_2$Fe]$^+$; published: $E_{1/2} = -0.07$ V vs. [Cp*$_2$Fe]/[Cp*$_2$Fe]$^+$, or ca. −0.50 V vs. [Cp$_2$Fe]/[Cp$_2$Fe]$^+$ after correction).[6c] This event was attributed by the authors to a one-electron oxidation on the basis of DFT calculations, and also seems consistent with the unique stability of the [M(CAAC)$_2$]$^{n+}$ system in oxidation states between those usually expected for the metals.[3–8] In contrast, the remaining complexes all showed irreversible oxidation waves (**2**: $E_{pa} = -0.09$ V; **3**: $E_{pa} = -0.11$ V; [Pt(PCy$_3$)$_2$]: $E_{pa} = 0.00$ V; [Pt(P*i*Pr$_3$)$_2$]: $E_{pa} = +0.12$ V). If we set aside the unique behavior of **1**, we can infer slightly stronger reductive ability of compounds **2** and **3** compared to the two homoleptic bis(phosphine) complexes. However, as was spectroscopically and crystallographically demonstrated above, higher electron density does not always translate faithfully into stronger Lewis basicity.

UV/Vis spectroscopy

The origin of the orange color of **1–3** is evident from their UV/Vis spectra (recorded in benzene, Figure 4, top; Table 1), which contain multiple excitations tailing off in the region $\lambda = 430$–530 nm. In contrast, the longest wavelength bands of [Pt(P*i*Pr$_3$)$_2$] and [Pt(PCy$_3$)$_2$] can be found at $\lambda = 393$ and 395 nm,

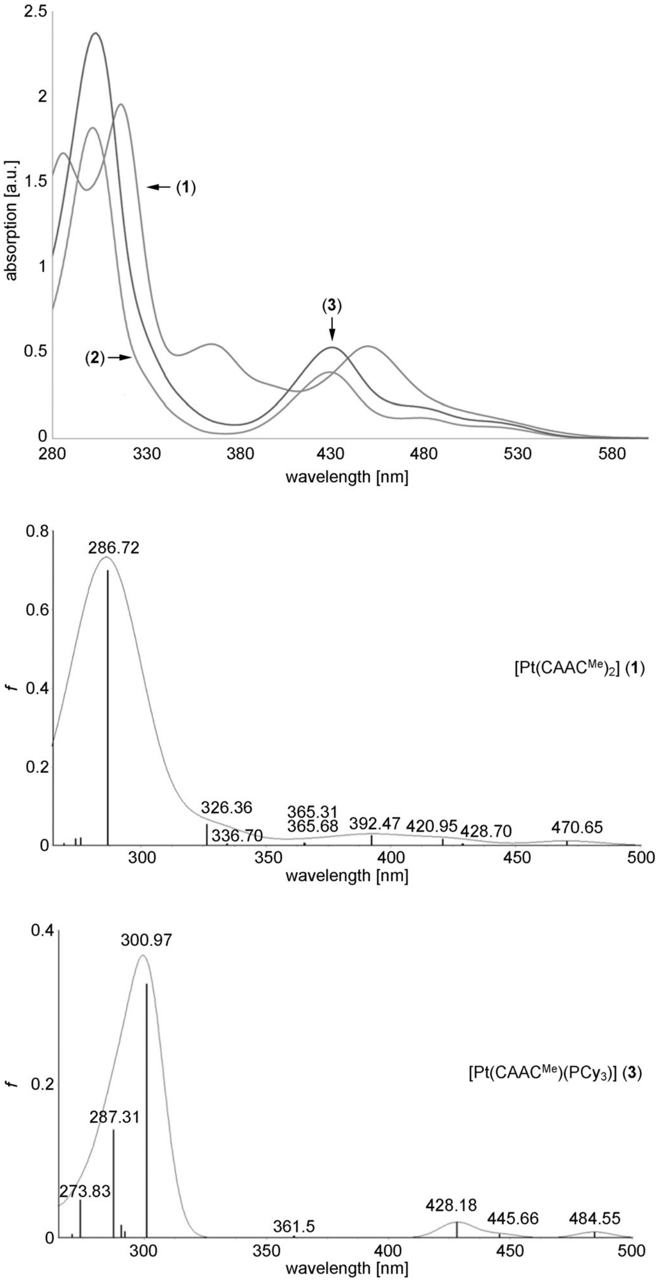

Figure 4. Top: Experimental UV/Vis spectra of **1**–**3**. Middle and bottom: Calculated UV spectra of **1** and **3** at the PCM-CAM-B3LYP/def2-SVP//PCM-B3LYP/def2-SVP level.

Table 1. UV/Vis peak list for **1**–**3**, [Pt(P*i*Pr$_3$)$_2$] and [Pt(PCy$_3$)$_2$]. Spectra were recorded in benzene.

Compd.	λ [nm]
1	285.5, 317.0, 365.0, 449.5
2	243.5, 301.5, 429.5, 479.5, 516.0
3	303.5, 431.0, 473.5
[Pt(P*i*Pr$_3$)$_2$]	247.0, 258.5, 315.5, 342.0, 395.0
[Pt(PCy$_3$)$_2$]	247.5, 258.5, 316.0, 339.5, 393.0

respectively, which explains their light yellow color (Figure S2 the Supporting Information).

DFT Calculations

Optimized geometries of **1** and **3** were calculated at the BP86/def2-TZVPP level (see the Supporting Information). The calculated Pt–C distances of **1** are slightly longer than those found experimentally (X-ray **1**·C_6H_6: 1.965(2), 1.969(2) Å; calcd **1**: 1.993 Å), whereas the calculated C-Pt-C angle is slightly smaller than the experimental value (X-ray **1**·C_6H_6: 171.13(7)°; calcd **1**: 169.4°). Notably, the calculated alignment of the CAAC ligands around the C-Pt-C axis agrees much better with our experimentally derived value than with the published structure,[6c] both in terms of N-C-C-N torsion angle (X-ray **1**·C_6H_6: 73.1°; X-ray **1**·0.5 THF: 48.7°; calcd **1**: 80.4°) and the angle between the least-squares planes of the CAAC heterocycles (X-ray **1**·C_6H_6: 70.0°; **1**·0.5 THF: 30.3°; calcd **1**: 74.5°). Although the crystallographically determined structure of **3** is too imprecise to discuss in detail, the calculated geometry of **3** (Pt–C 1.984 Å) shows a slightly shorter Pt–C distance than that calculated for **1**. The HOMOs of both **1** and **3** are effectively the set of five d orbitals; however, some metal-to-ligand π-backbonding interactions are suggested by the HOMO−3 and HOMO−4 levels in both compounds, which show π interactions between the ligands and the d_{yz} and d_{xz} orbitals (see the Supporting Information for frontier orbital depictions). The extent of ground state π backbonding is evident from the fact that π symmetry HOMO−3 and HOMO−4 are stabilized by approximately 0.6 eV with respect to the δ symmetry (non-bonding) HOMO−1 and HOMO−2 pure Pt d orbitals.

TD-DFT calculations were undertaken to explain the orange color of **1** and **3**, which was surprising given that the homoleptic complexes $[\mathrm{Pt}(\mathrm{P}i\mathrm{Pr}_3)_2]$ and $[\mathrm{Pt}(\mathrm{PCy}_3)_2]$ are only very slightly colored (light yellow). The calculated UV/Vis absorption spectra of **1** and **3** (TD-PCM-CAM-B3LYP/def2-SVP, see the Supporting Information for details) reproduce the gross structure of the experimental absorption spectra well (Figure 4). There is a shoulder between $\lambda = 480$–530 nm in the experimental spectrum of **1**, which has been reproduced at 470.65 nm and resulted from an excitation mainly from HOMO to LUMO (Table 2). There is an experimental band at 449.5 nm, which was reproduced with an approximately 55 nm blueshift at 392.47 nm with two shoulders at 428.70 and 420.95 nm. The excitation at 473.5 nm of **3** was reproduced at 484.55 nm, which results from an excitation from mainly HOMO to LUMO (Table 2). The excitation at 431.0 nm was reproduced at 428.18 nm with a shoulder at 445.66 nm. The low-energy calculated excitations of **1** (470.65, 428.70, and 420.95 nm) and **3** (484.55, 445.66, and 428.18 nm) are presumably the cause of the orange color of the complexes. These transitions are all dominated by excitations into the LUMO of each complex, effectively a ligand-centered π^* orbital, with antibonding interactions between C^{carbene} and N (see the Supporting Information for frontier orbital depictions). This suggests to us that the presence of the low-lying empty π^* orbital, responsible for the strong π-acceptor properties of the CAAC ligand in the ground state, is also the predominant cause of the weak, low-energy absorptions in the blue region of the visible spectra of **1** and **3**, and thus also the unusual orange colors of the complexes.

Table 2. TD-DFT-computed transitions of **1** and **3**.

	λ [nm]	From:	To:	Contribution [%]	Oscillator strength
1	470.65	HOMO−2	LUMO	8.9	0.0120
		HOMO	LUMO	84.8	
		HOMO	LUMO+4	3.3	
	428.70	HOMO−1	LUMO	91.0	0.0020
		HOMO−1	LUMO+4	3.9	
	420.95	HOMO−2	LUMO	85.3	0.0166
		HOMO−2	LUMO+4	3.7	
		HOMO	LUMO	8.8	
	392.47	HOMO−1	LUMO	2.2	0.0262
		HOMO	LUMO+1	52.1	
		HOMO	LUMO+2	3.4	
		HOMO	LUMO+5	35.5	
3	484.55	HOMO−2	LUMO	11.5	0.0076
		HOMO	LUMO	83.6	
	445.66	HOMO−2	LUMO	2.6	0.0050
		HOMO−1	LUMO	93.0	
		HOMO−1	LUMO+2	2.4	
	428.18	HOMO−2	LUMO	81.3	0.0202
		HOMO−2	LUMO+2	2.0	
		HOMO−1	LUMO	2.0	
		HOMO	LUMO	11.4	

Conclusion

An improved synthetic route to the recently published homoleptic complex $[\mathrm{Pt}(\mathrm{CAAC}^{\mathrm{Me}})_2]$ and convenient routes to new heteroleptic complexes of the form $[\mathrm{Pt}(\mathrm{CAAC})(\mathrm{PR}_3)]$ were presented. Although the homoleptic complex was found to be inert to many reagents, oxidative addition and metal-only Lewis pair (MOLP) formation was observed from one of the heteroleptic complexes. The homoleptic $[\mathrm{Pt}(\mathrm{CAAC})_2]$ and heteroleptic $[\mathrm{Pt}(\mathrm{CAAC})(\mathrm{PR}_3)]$ complexes are quite similar in their spectroscopic and structural properties, yet their electrochemical behavior and reactivity differ greatly. The different electrochemical behavior can be attributed to the unique ability of the CAAC ligands of the $[\mathrm{M}(\mathrm{CAAC})_2]^{n+}$ arrangement to accept a single electron, whereas the lower reactivity of $[\mathrm{Pt}(\mathrm{CAAC}^{\mathrm{Me}})_2]$ is presumably a simple steric effect. The unusually strong color of the CAAC-containing Pt^0 complexes was investigated by TD-DFT calculations and attributed to excitations to the LUMOs of the complexes, which are predominantly ligand-based π^* orbitals.

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Keywords: carbenes · Lewis bases · oxidative addition · phosphine ligands · platinum

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