Organometallic Complexes

A Simple Approach to Room Temperature Phosphorescent Allenylidene Complexes**

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Owing to their potential application in optoelectronic devices, organometallic complexes containing a linear π-conjugated carbon chain have attracted much attention for more than twenty years.[1] In allenylidene complexes, $[L_nM=C=C=C(R^1)R^2]$, the presence of π interactions between the metal ion and the rigid, linear allenylidene bridge results in interesting electronic communication between the two terminal groups; therefore, these metal complexes appear to be good candidates for molecular wiring.[2] For example, Wong et al. reported a dinuclear ruthenium unit, {Ru=C=C=C(2-py)₂Ru}, displaying intense infrared absorption attributed to the delocalization of the electron density over both ruthenium ions and the allenylidene bridge.[3]

Photoluminescence is another important aspect of organic materials for optoelectronic applications. However, allenylidene complexes that emit at room temperature have never been described. To our knowledge, there is only one report of emission at 77 K for allenylidene complexes $[Cl(dppm)_2Ru=C=C=C(R^1)R^2]$, where dppm is bis(diphenylphosphino)methane.[4] Ruthenium allenylidene complexes of the type $[(phen)(Me_3tacn)Ru=C=C=C(R^1)R^2]$ (where phen = 1,10-phenanthroline and Me₃tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) show no emission, neither at room temperature nor at low temperature, in contrast to their corresponding substituted carbene complexes which emit at 77 K.[5]

Herein, we report a simple strategy for the preparation of stable allenylidene iridium complexes containing bis-cyclometalated ligands, which are phosphorescent at room temper-

ature. The resulting complex **3-PF₆** emits at 464 nm with a photoluminescence quantum yield (Φ) of 2.9% in acetonitrile.

The synthesis and isolation of the first allenylidene complexes was simultaneously reported in 1976 by Fischer et al. (M = Cr, W)[6] and Berke (M = Mn).[7] Allenylidene complexes of many transition metals have since been prepared and their chemistry and catalytic activity reviewed.[8] The iridium-containing cumulenes reported to date have been based on square-planar iridium(I) central ions.[9] To prepare an octahedral iridium(III) allenylidene complex, we first synthesized and isolated the alkynyl intermediate **2** (Scheme 1a). Although many platinum[10]
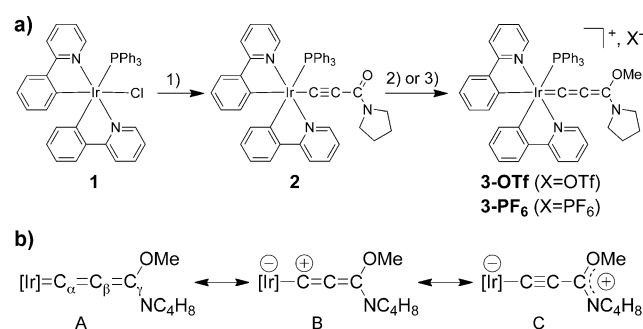
Scheme 1. a) Synthesis of alkynyl and allenylidene complexes. Reagents: 1) Ag-C≡C−C(=O)N(CH₂)₄, 2) MeOTf, 3) MeOTf then KPF₆; b) resonance forms of allenylidene complexes.

and gold[11] alkynyl complexes have been reported, surprisingly the corresponding iridium complexes have not been explored, with only one preparation of phosphorescent alkynyl iridium complexes with a terdentate ligand reported.[12] Another publication addressed theoretical investigations of the same class of compounds.[13]

Complex **1**, [Ir(ppy)₂(PPh₃)Cl], was prepared according to classical methods (see Supporting Information for details). To prepare the alkynyl and allenylidene complexes (Scheme 1a), we used a slightly modified version of the route described in the literature.[14] Complex **1** was reacted overnight with silver propiolamide in 1,2-dichloromethane. After filtration through celite to remove silver chloride and purification by column chromatography, the pure iridium alkynyl complex **2** was obtained in 67% yield as a yellow solid. Alkylation with methyl triflate (MeOTf) in CH₂Cl₂ at room temperature followed by column chromatography gave complex **3-OTf**. Complex **3-PF₆** was prepared in a similar manner, where the crude product was extracted with aqueous KPF₆ solution

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three times to exchange the anion (X) from triflate to hexaflurophosphate.

The ^1H NMR spectrum of **2** exhibits two signals for the two N-bound $-CH_2-$ groups, indicating a rather high barrier to rotation around the $C(sp^2)-N$ bond. The resonances of the alkynyl ligand in the ^{13}C NMR spectra compare well with those of palladium alkynyl complexes.[14] The formation of the cationic allenylidene complexes by alkylation of the alkynyl complexes was accompanied by a pronounced (approximately 50 ppm) downfield shift of the C_α resonance, an approximately 8 ppm upfield shift of the C_β resonance, and a shift of the IR $\nu(C\equiv C)$ vibration to lower energy by 18 cm^{-1}. The resonances of the C_γ atom and the $N-CH_2$ groups were almost unaffected by the alkylation. Similar trends have been found for alkylation of palladium alkynyl complexes.[14] The extent of these shifts and the detection of two resonances for the $N-CH_2$ groups in the ^1H and ^{13}C NMR spectra demonstrate the importance of the zwitterionic resonance forms B and C for the overall bond description of these cationic allenylidene complexes (Scheme 1b). The barrier to rotation around the $C(sp^2)-N$ bond in the allenylidene complex **3-PF$_6$** is high. No coalescence of the $N-CH_2$ signals was detected up to the instrumental limit of 120 °C, indicating considerable C–N double-bond character and a rather important contribution of the resonance form C (Scheme 1b). A comparison of the spectroscopic data of these cationic iridium allenylidene complexes with those of the related cationic palladium and platinum complexes [Br(PPh$_3$)$_2$M=C=C=C(OMe)N-(CH$_2$)$_4$][OTf] where M = Pd, Pt,[14] reveals that the alkynyl character of the iridium allenylidene complexes (see C in Scheme 1b) is significantly more pronounced than in the corresponding group ten complexes, as evidenced by the $\nu(C\equiv C)$ vibration at higher energy by about 60 cm^{-1}.

The X-ray crystal structures of complex **2** and **3-PF$_6$** have been obtained from single crystals, grown by slow diffusion of heptane into a CH$_2$Cl$_2$ solution of the complex (Figure 1). The complexes show near-octahedral geometry with the two pyridines of the anionic cyclometalated ligands in the *trans* position to one another and the two orthometalated phenyl rings in the *cis* position, retaining the geometry of the starting chloro-bridged iridium dimer. In both complexes, the Ir–C$_3$
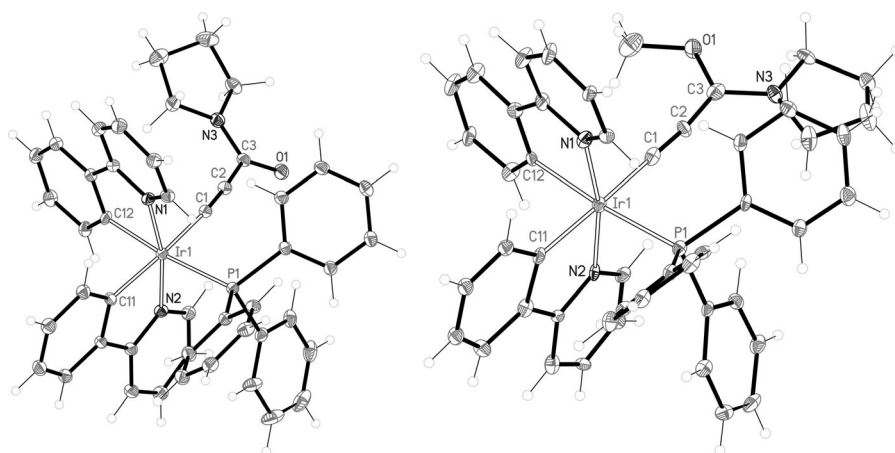
Table 1: Selected distances and angles for complexes **2** and **3-PF$_6$** from X-ray crystal structures and theoretical calculations (DFT/M06).[15]

	2	**3-PF$_6$**	**2**	**3-PF$_6$**
		experimental		theoretical
Distances [Å]				
Ir–C1	2.061(4)	2.001(17)	2.059	2.007
C1–C2	1.204(5)	1.24(2)	1.222	1.234
C2–C3	1.449(5)	1.38(2)	1.436	1.380
Ir–P	2.3821(10)	2.406(3)	2.454	2.465
Angles [°]				
Ir–C1–C2	168.8(3)	174.9(13)	168.1	174.9
C1–C2–C3	174.5(4)	172.2(18)	169.0	171.9
C2–C3–O1	122.9(4)	123.8(15)	122.0	122.3
C2–C3–N3	115.0(3)	126.1(16)	116.3	123.0

chain is slightly bent: Ir–C1–C2 = 168.8(3)° (**2**) and 174.9(13)° (**3-PF$_6$**), C1–C2–C3 = 174.5(4)° (**2**) and 172.2(18)° (**3-PF$_6$**; see Table 1 and the Supporting Information for more details). However, a modest deviation from linearity of the M–C$_3$ fragment in allenylidene complexes is often seen. The Ir–C1 bond in the cationic allenylidene complex (**3-PF$_6$**) is significantly shorter than in the neutral alkynyl complex (**2**). This double-bond character is attributed to the increased π-back-bonding from the metal to the ligand upon alkylation and is accurately reproduced by theoretical calculations. In addition, as expected, the C1–C2 bond of **3-PF$_6$** becomes longer (less triple-bond character than in **2**) and the C2–C3 bond shortens. Theoretical geometries for both complexes agree well with experiment, further highlighting the changes in bond character occurring between the alkynyl and allenylidene complex (Table 1).

The electrochemical potentials versus ferrocenium/ferrocene (Fc$^+$/Fc) of **2** and **3-PF$_6$** were measured using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as supporting electrolyte in acetonitrile and are 0.68 V (**2**) and 0.91 V (**3-PF$_6$**) for the oxidation (irreversible) and −2.57 V (**2**) and −2.22 (**3-PF$_6$**) for the reduction (irreversible; Table 2). The oxidation and reduction potentials of the cationic complex **3-PF$_6$** are shifted towards a more positive value compared to complex **2**, pointing to an increased π-back-bonding donation to the allenylidene wire. A difference of 0.34 eV is theoretically computed between the ionization energy of **3-PF$_6$** and **2**, in good agreement with the experimentally measured 0.23 eV between the two respective redox potentials.

The UV/Vis absorption spectra of **2** and **3-PF$_6$**, recorded in acetonitrile solution, are reported in Figure 2. They display intense absorption bands (ε ≈ 50 000 M^{-1}cm^{-1}) in the UV region, assigned to ligand-centered (LC) π–π* transitions involving the cyclometalated ligand 2-phenylpyridine. The weaker (ε ≈ 5000 M^{-1}cm^{-1}) bands at lower energies (350–440 nm) are attributed to

Figure 1. ORTEP drawing of the X-ray crystal structure of **2** (left) and **3-PF$_6$** (right).

Table 2: Electrochemical and photophysical data for complexes **2** and **3-PF$_6$** in acetonitrile.

	2	3-PF$_6$
E_{ox}[a]	0.68 V	0.91 V
E_{red}[a]	−2.57 V	−2.22 V
λ_{max} (RT)	474 nm	464 nm
λ_{max} (77 K)	464 nm	463 nm
Φ	3.5%	2.9%
τ	253 ns	465 ns
k_r[b]	1.38×10^5 s^{-1}	0.62×10^5 s^{-1}
k_{nr}[b]	38.1×10^5 s^{-1}	20.9×10^5 s^{-1}

[a] versus Fc$^+$/Fc with 0.1 M TBAPF$_6$ as supporting electrolyte. [b] Radiative constant: $k_r = \tau^{-1}$; nonradiative constant: $k_{nr} = \tau^{-1} - k_r$ (assuming unitary intersystem crossing efficiency).
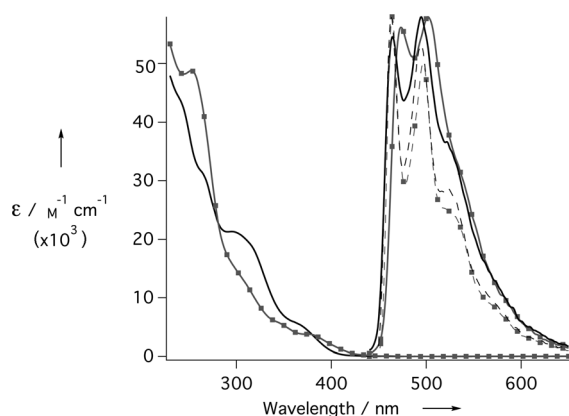

Figure 2. Absorption and emission spectra of **2** (squares) and **3-PF$_6$** (no squares) at room temperature (solid line) and 77 K (dashed line).

metal-to-ligand charge-transfer (MLCT) transitions. The first singlet-to-singlet vertical transitions are computed at 377 nm (**3-PF$_6$**) and 389 nm (**2**). Strong HOMO→LUMO character (85%) is seen for **2**, promoting an electron mostly localized in a 5d(Ir) + phenyl orbital to one located on the ppy ligand. The transition of **3-PF$_6$** can also largely (77%) be described as HOMO→LUMO excitation and, therefore, populates an orbital localized on the allenylidene ligand with weak contributions on the ppy ligands (see Supporting Information). Finally, the weak absorption bands ($\varepsilon \approx 30$–70 M^{-1}cm^{-1}) detected at 454 nm for **3-PF$_6$** and 460 nm for **2** correspond to direct singlet-triplet transitions. Triplet states are theoretically located at 442 nm for **3** and 448 nm for **2**, and they can be assigned to MLCT transitions towards ppy ligands. Interestingly, the allenylidene ancillary ligand of **3** does not seem to play an important role for these specific triplet states, unlike for the singlet MLCT states (see Supporting Information). This result suggests that the emission profiles of both compounds (**2** and **3**) should not differ strongly, in contrast to their absorption profiles.

When the acetonitrile solutions of the complexes are excited within the π–π* and MLCT absorption bands, the complexes show structured emission with maxima at 474 nm for **2** and 464 nm for **3-PF$_6$** (Figure 2 and Table 2). Complex **2** exhibits a Φ of 3.5% and excited-state lifetimes (τ) of 253 ns,

whereas for complex **3-PF$_6$** the Φ is 2.9% and τ is 465 ns. At 77 K, the emission spectra show intense and highly resolved bands with very small rigidochromism compared to room-temperature emission (Figure 2). In addition to the small Stokes shift, of about 10 nm, these results point to a weak MLCT character of the triplet excited state, which is therefore largely of ligand-centered character. To verify the emission character of **3**, ΔSCF (delta self-consistent field; see Supporting Information) calculations based on the M05-2X functional[16] were performed between the first triplet state (T$_1$) and the singlet ground state. At the optimized geometry of T$_1$, the calculated emission lies at 2.50 eV, which is in good agreement with the experimental value at 77 K (2.68 eV). Owing to the strong localization of the spin density on a ppy ligand (Figure 3), the character of the emission of both compounds **2** and **3** corresponds mostly to an LC transition with a small amount of MLCT, as postulated from the experimental evidence.
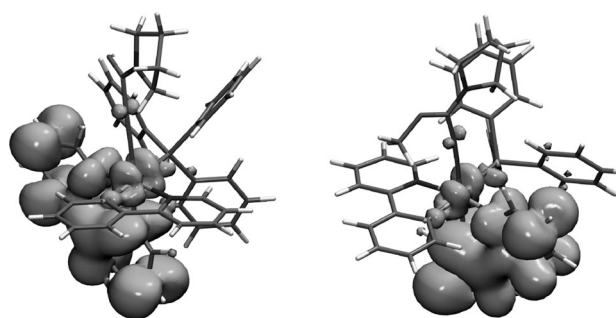

Figure 3. Spin density for the UDFT/M05-2X geometry-optimized first triplet state of **2** (left) and **3** (right). Isovalue = 0.0007.

In conclusion, we report stable room-temperature phosphorescent alkynyl and allynylidene complexes. Our approach uses the excellent photophysical properties of bis-cyclometalated iridium complexes. To our knowledge, these results represent the first bis-cyclometalated iridium complexes with alkynyl and allenylidene ligands. Furthermore, this is the first allenylidene complex that emits at room temperature. This new class of compounds provides new opportunities for the application of allenylidene complexes in the field of organic optoelectronics.

Experimental Section

2: A solution of [(ppy)$_2$Ir(PPh$_3$)Cl] (136 mg, 0.17 mmol) and Ag-C≡C−C(=O)N(CH$_2$)$_4$ (43 mg, 0.19 mmol) in 1,2-dichloroethane (15 mL) was stirred at room temperature overnight. The mixture was filtered through celite to remove silver residues; the celite was washed with CH$_2$Cl$_2$ and the solvent removed under vacuum. The residue was purified by column chromatography on silica gel using CH$_2$Cl$_2$/acetone 2:1. After evaporation of the solvent the pure product was obtained as a yellow solid. Yield: 101 mg (0.11 mmol, 67%). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 9.21$ (d, $^3J_{H,H} = 5.8$ Hz, 1H, ArH), 8.63 (d, $^3J_{H,H} = 5.8$ Hz, 1H, ArH), 7.85 (d, $^3J_{H,H} = 8.1$ Hz, 1H, ArH), 7.64 (t, $^3J_{H,H} = 7.4$ Hz, 1H, ArH), 7.55 (d, $^3J_{H,H} = 7.8$ Hz, 1H, ArH), 7.50 (d, $^3J_{H,H} = 7.8$ Hz, 1H, ArH), 7.44 (t, $^3J_{H,H} = 7.4$ Hz, 2H, ArH), 7.31 (t, $^3J_{H,H} = 9.0$ Hz, 6H, ArH), 7.20 (t, $^3J_{H,H} = 6.9$ Hz, 3H, ArH), 7.10 (td,

$^3J_{H,H} = 7.7$ Hz, $^4J_{H,H} = 1.5$ Hz, 6H, ArH), 6.81 (t, $^3J_{H,H} = 7.5$ Hz, 2H, ArH), 6.67 (q, $^3J_{H,H} = 7.1$ Hz, 2H, ArH), 6.61 (q, $^3J_{H,H} = 6.8$ Hz, 2H, ArH), 6.11 (d, $^3J_{H,H} = 7.4$ Hz, 1H, ArH), 5.93–5.90 (m, 1H, ArH), 3.26 (t, $^3J_{H,H} = 6.9$ Hz, 2H, NCH$_2$), 2.88–2.77 (m, 2H, NCH$_2$), 1.67 (quint, $^3J_{H,H} = 6.8$ Hz, 2H, CH$_2$), 1.51 ppm (quint, $^3J_{H,H} = 6.7$ Hz, 2H, CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 169.2$ (d, $J = 6.0$ Hz), 168.4 (C$_\gamma$), 165.3 (d, $J = 6.6$ Hz), 161.8, 160.8, 155.5, 154.7, 153.8, 144.6, 142.7, 136.0, 135.7, 134.7 (d, $J = 9.7$ Hz, PPh$_3$), 133.0, 131.7, 131.3, 129.8 (d, $J = 12.2$ Hz, PPh$_3$), 129.4 (PPh$_3$), 127.8 (d, $J = 8.9$ Hz, PPh$_3$), 123.8, 123.7, 122.3, 121.8, 121.5, 121.3, 119.4, 118.8 (d, $J = 11.0$ Hz, C$_\alpha$), 118.2, 105.4 (C$_\beta$), 47.4 (NCH$_2$), 44.8 (NCH$_2$), 25.5 (CH$_2$), 25.1 ppm (CH$_2$); ^{31}P NMR (81 MHz, CDCl$_3$): $\delta = -3.5$ ppm (s, PPh$_3$); IR (neat): ν(C≡C) = 2080 cm^{-1}; HRMS (ESI-TOF): *m/z* (%): calcd: 886.2542; found: 886.2543 (100) [M^+]. Elemental analysis calcd (%) for C$_{47}$H$_{39}$IrN$_3$OP·0.33 CH$_2$Cl$_2$: C 62.25, H 4.38, N 4.60; found: C 62.28, H 4.76, N 4.34. CCDC 878944 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3-PF$_6$: A CH$_2$Cl$_2$ solution of **2** (200 mg, 0.23 mmol) was degassed by five vacuum and back-fill (N$_2$) cycles. MeOTf (28 μL, 0.25 mmol, 1.1 equiv.) was added and the mixture stirred at room temperature for two hours. Additional MeOTf (28 μL) was added and the mixture stirred at room temperature overnight. The crude reaction mixture was extracted with aqueous KPF$_6$ solution (3×). The combined organic layers were dried over MgSO$_4$ and the volatiles removed under vacuum. The crude product was purified by column chromatography on silica using CH$_2$Cl$_2$/acetone 20:1. After evaporation of the solvent, the pure product was obtained as a yellow solid. Yield: 179 mg (0.18 mmol, 74%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 8.96$ (d, $^3J_{H,H} = 5.6$ Hz, 1H, ppy), 8.65 (d, $^3J_{H,H} = 5.6$ Hz, 1H, ppy), 7.98 (d, $^3J_{H,H} = 7.6$ Hz, 1H, ppy), 7.84 (t, $^3J_{H,H} = 7.2$ Hz, 1H, ppy), 7.65 (d, $^3J_{H,H} = 8.0$ Hz, 1H, ppy), 7.61–7.53 (m, 3H, ppy), 7.32 (td, $^3J_{H,H} = 7.2$ Hz, $^4J_{H,H} = 1.2$ Hz, 3H, PPh$_3$), 7.22 (td, $^3J_{H,H} = 7.8$ Hz, $^4J_{H,H} = 2.0$ Hz, 6H, PPh$_3$), 7.14 (t, $^3J_{H,H} = 8.4$ Hz, 6H, PPh$_3$), 6.98 (t, $^3J_{H,H} = 7.6$ Hz, 1H, ppy), 6.93 (t, $^3J_{H,H} = 7.2$ Hz, 1H, ppy), 6.87–6.83 (m, 1H, ppy), 6.82–6.79 (m, 1H, ppy), 6.75 (t, $^3J_{H,H} = 7.4$ Hz, 1H, ppy), 6.11–6.08 (m, 1H, ppy), 5.89 (d, $^3J_{H,H} = 7.6$ Hz, 1H, ppy), 3.56 (s, 3H, OMe), 3.50 (t, $^3J_{H,H} = 7.0$ Hz, 2H, NCH$_2$), 3.05 (t, $^3J_{H,H} = 7.0$ Hz, 2H, NCH$_2$), 1.98–1.88 (m, 2H, CH$_2$), 1.79–1.67 ppm (m, 2H, CH$_2$); ^{31}P NMR (81 MHz, CD$_2$Cl$_2$): $\delta = -3.0$ (s, PPh$_3$), -144.5 ppm (sept, $^1J_{PF} = 710$ Hz, PF$_6$); ^{19}F NMR (188 MHz, CD$_2$Cl$_2$): $\delta = -73.5$ ppm (d, $^1J_{PF} = 709$ Hz, PF$_6$); IR (neat): ν(C≡C) = 2062 cm^{-1}; HRMS (ESI-TOF): *m/z* (%): calcd 900.2698; found 900.2681 (100) [$(M-\text{PF}_6)^+$]. Elemental analysis calcd (%) for C$_{48}$H$_{42}$F$_6$IrN$_3$OP$_2$·0.25 CH$_2$Cl$_2$: C 54.35, H 4.02, N 3.94; found: C 54.38, H 3.96, N 3.84. CCDC 878945

(**3-PF$_6$**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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