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COMMUNICATION

Charge-induced facial-selectivity in the formation of new cationic planar chiral iridacycles derived from aniline[†]

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The reaction of chiral chlorido-iridacyclic 2-(4-*N*,*N*-dimethylaminophenyl)pyridines with solvato-type $[Cp*M(S)_3]^{q+}$ (M = Ru, S = MeCN, q = 1; M = Ir, S = MeC(O)Me, q = 2) complexes produces new cationic racemic planar chiral iridacycles in an efficient and diastereospecific way.

In spite of the growing interest¹ in the use of planar chiral metallacycles² as catalysts, the majority of reports deal exclusively with complexes of square-planar (SP-4) Pd or Pt centres.^{3,4} By expanding the variety of coordination geometries at the chelated metal centre to octahedral (OC-6) and pseudo-tetrahedral (T-4) one would not only open up new horizons but also introduce the major issues of stereospecificity and conformational instability at the stereogenic centres.⁴ Planar-chiral metallacycles can be synthesized mainly by two methods;⁴ *i.e.* the cyclometalation of a planar pro-chiral ligand and the π -coordination of an unsaturated metal moiety to a preformed metallacycle.⁵ The predominant role of Coulomb repulsion between ligands rationalized the high stereospecificity of the cyclometalation reaction of π -Cr(CO)₃ complexes used as ligands by pseudo-tetrahedral (T-4) and octahedral (OC-6)centres.^{6,7} Charged (cationic or anionic) planar chiral analogues constitute a class of organometallic compounds of high value because their resolution into enantio-enriched compounds should be readily achievable in principle.⁸ Surprisingly, only complexes of SP-4 chelates have been reported in the literature so far.^{5,9–11} In this communication, we disclose the efficient and stereospecific syntheses of unprecedented cationic and binuclear planar chiral iridacycles from the face-selective π -coordination of an electron-rich aniline-derived ligand with cationic metal centres. Dynamic variable temperature ¹H NMR experiments, backed with thorough DFT investigations, further

confirms the essential role of the $-NMe_2 \text{ group}^{11}$ in the consolidation of the π -metal bonding, particularly in bis-cationic complexes.

The starting metallacycles used in this study were synthesized by the reaction of ligands $1a^{11}$ and **b** with $[Cp*IrCl_2]_2^{12}$ in CH₂Cl₂ in the presence of hydrated NaOAc at room temperature.¹³ The resulting racemic Ir(III) complexes 2aand **b** were used in subsequent reactions with solutions of $[Cp*Ru(MeCN)_3][PF_6]^{14}$ and $\{Cp*Ir[Me_2C(O)]_3\}[PF_6]_2^{15}$ (Scheme 1). In all cases, according to X-ray diffraction analysis, the products of the reaction with these cationic reagents possess *endo* stereochemistry (Scheme 1), *i.e* the geometry wherein the Ir-bound chlorido ligand and the π -bonded metal moiety are in a *syn* relationship with respect to the mean plane of the chelate.

The structures[‡] of complexes **2a**, [*endo*-**3a**][PF₆]₂ and [*endo*-**4a**][PF₆] are displayed in Fig. 1. Notably, the synthesis of the corresponding neutral, Cr(CO)₃-containing analogs yielded, as expected,⁷ the *exo* stereoisomers [*exo*-**5a** and **b**]. This was the case regardless of the synthetic method chosen, *i.e.* either the direct ligand exchange reaction of **2b** with $(\eta^6$ -naphthalene)Cr(CO)₃¹⁶ (quantitative) or the cycloiridation⁷



Scheme 1 The syntheses of compounds 2a and b, $[endo-3a][PF_6]_2$, $[endo-4a][PF_6]$ and [exo-5a and b].

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[†] Electronic supplementary information (ESI) available: (1) full experimental procedures and analytical data, (2) extensive crystallographic information, (3) dynamic ¹H NMR data, (4) full computational details with references and (5) cartesian coordinates for optimized geometries of **II–V**, [*endo-3a*]²⁺ and their associated rotational transition states **TS1-2**. CCDC 805113–805116. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc05711h



Fig. 1 ORTEP-type drawings of the structures of (a) 2a, (b) [endo-3a]²⁺,
(c) [endo-4a]⁺, (d) [exo-5b] with partial atom numbering. Ellipsoids were drawn at a 30% probability level. Hydrogen atoms and molecules of solvent were omitted for the sake of clarity.

of ligands 1c and d (76 and 72% isolated yield, respectively) in the conditions used for the synthesis of 2a and b. Table 1 provides a selection of geometric parameters for 2a, [endo-3a][PF₆]₂, [endo-4a][PF₆] and [exo-5b]. The slight variation of $d_{\rm Cl}$ is worthy of note, as it varies in response to the electronwithdrawing effect of the π -bonded metal, *i.e.* by shortening the Ir–Cl distance following the order $2a > exo-5b \sim endo-4a >$ endo-3a. The distance separating the ipso position bearing the amino group and the π -bound metal, *i.e.* $d_{\rm M}$, formally increases as the charge of the complex increases. As expected, longer $d_{\rm M}$ and shorter $d_{\rm N}$ distances are observed for the bis-iridium complex [endo-3a]²⁺. Table 1 lists geometrical parameters selected from the relaxed gas-phase geometries of models of the compounds addressed herein, i.e. II-V. For practical reasons, the Cp* ligand was replaced by Cp, which does not greatly affect the overall analysis of the stereo-electronic

Table 1 A list of selected experimental[‡] (arabic numbers) and theoretical (roman numerals) interatomic distances (Å) and intraannular angles α (°). Wiberg bond indices (wbi) are provided for the computed model geometries (*cf.* ESI[†] for full computational details)

| Me dh Me d | | -∟ | 9 N II II V | lodels , {M} = l, {M} : /, {M} , {M} = | ; = nil, L= Cp, = IrCp, L= (= RuCp, L= = Cr(CO) ₃ , I | , <i>q</i> = 0 Cp, <i>q</i> = ⊧ Cp, <i>q</i> L= Cp, | +2 = +1 q= 0 |
|--|---|--------------------------|--|--|---|--|--|
| Cmpd | $d_{\rm M}{}^a$ | wbi ^b | $d_N^{\ a}$ | wbi ^b | $d_{\rm Cl}{}^a$ | wbi ^b | α^{a} |
| $\begin{array}{c} 2a \\ II^{a} \\ [endo-3a]^{2+} \\ III^{a} \\ [endo-4a]^{+} \\ IV^{a} \\ [exo-5b] \\ V^{a} \end{array}$ | 2.444(3) 2.524 2.325(3) 2.387 2.359(5) 2.391 | 0.09 0.18 0.14 | 1.379(3) 1.387 1.326(7) 1.335 1.378(4) 1.371 1.366(6) 1.375 | 1.15 1.35 1.19 1.18 | 2.4122(6) 2.401 2.373(2) 2.388 2.387(4) 2.398 2.402(1) 2.407 | 0.52 0.50 0.51 0.51 | 118.0(2) 118.9 114.6(5) 112.2 117.5(3) 116.1 117.2(2) 117.3 |

^{*a*} Calculated from relaxed gas-phase geometries. ^{*b*} Computed from the natural atomic orbital basis (NAO) for relaxed gas-phase geometries.

effects.¹⁷ The model of [*exo*-**5b**], *i.e.* V, was also simplified by replacing the *t*Bu group by H. The set of gas phase model geometries II–V reproduces the trends observed in the experimental structures; the distance $d_{\rm M}$ increases in the order [*endo*-**4a**]⁺ ~ [*exo*-**5b**] < [*endo*-**3a**]²⁺ and $d_{\rm N}$ decreases in the order **2a** ~ [*endo*-**4a**]⁺ ~ [*exo*-**5b**] > [*endo*-**3a**]²⁺.

These observations suggest that the increase in the double bond character for the Me₂N–C_{*ipso} bond in* $[endo-3a]^{2+}$ is a</sub> response to the major electron density withdrawal operated by the Cp*Ir moiety; the Wiberg bond indices (wbis) for the Me₂N-C_{inso} bond of the models clearly support this assumption. Compared to that of II, the wbis for IV and V are only slightly larger by 0.03 units. For III the wbi indicates a net shift to some double bond character with a value of 1.35. Alternatively, analysis of the natural molecular orbitals (NMOs) indicates that there is no strong π -type donor-acceptor interaction between the nitrogen's lone pair and the arene's π -system. Natural population at the lone pair is evaluated to be ca. 1.66 e^- for II, IV and V, whereas for III it is 1.54 e^- . The Me₂N–C_{ipso} bond possesses a dominant σ character. The extent of the electron population "transfer" from the lone pair of NMe₂ to the rest of the molecule was qualitatively evaluated by using the rotamers resulting from the 90° rotation of the Me₂N group around the Cipso-N axis as reference structures. These structures are conformational transition states (Fig. 2, TS1 and TS2): the natural electron population at the lone pair rises to ca. 1.86 e⁻ for TS1-2_{II} and similar values are obtained for TS1-2_{III-V}. Consequently, upon relaxation of TS1-2 to the ground state (GS, Fig. 2), ca. 0.2 e⁻ in IV and V and ca. 0.3 e⁻ in III are being transferred to the rest of the molecule.

The most remarkable feature of $[endo-3a][PF_6]_2$ is the diastereotopicity of the methyl groups of the NMe2 substituent, which is expressed in the corresponding room temperature ¹H NMR spectra (CD_2Cl_2) by two distinct singlets appearing at $\delta 3.59$ and 3.46 ppm ($\Delta \delta (CD_2Cl_2) = 0.15$ ppm). This feature is not observed with the other complexes, which all display a single signal for the two methyls of the -NMe₂ group, from +20 °C down to -70 °C. It is worth noting that the inter-peak distance $\Delta \delta$ separating the two methyl singlets depends on the nature of the anions present in the solution; the same applies to the aromatic region. For $[endo-3a][ClO_4]_2 \Delta\delta(CD_2Cl_2) =$ 0.21 ppm. The barriers to rotation, *i.e.* ΔG_{rot} (T = 298.15 K), associated with the CAr-NMe2 rotor, were computed by considering the two possible orientations of the amino group depicted in TS1 and TS2 (Fig. 2). The ΔG_{rot} values computed for IV and V are comparable to that computed for II (Table 2). One can infer that the electronic effect of the π -bonded Cr(CO)₃ and CpRu⁺ (and by extension Cp*Ru⁺)



Fig. 2 Newman-type views of the singlet ground state (GS) and rotational transition states (TS1 and TS2).

Table 2 Theoretical and experimental Gibbs rotational barriers $(\Delta G_{\rm rot} \text{ in kcal mol}^{-1})$ at 298.15 K of the $-NMe_2$ group (see ESI† for full computational details)

| | Theory | Experiment | |
|-----------------------------|--------------------------------|---------------------------|-------------------------|
| Model/compound | $\Delta G_{\mathrm{rot1}}{}^a$ | $\Delta G_{\rm rot2}^{a}$ | $\Delta G_{ m rot}{}^a$ |
| $\overline{\mathbf{H}^{b}}$ | 6.6 | 6.6 | |
| \mathbf{III}^b | 21.3 | 20.9 | |
| \mathbf{IV}^b | 11.8 | 11.5 | |
| \mathbf{V}^{b} | 10.6 | 12.1 | |
| $[endo-3a]^{2+c}$ | 17.9 | 15.3 | $16.7(3)^d$ |

^{*a*} Calculated for T = 298.15 K. ^{*b*} Gas-phase relaxed structure. ^{*c*} COSMO (acetone) relaxed structure. ^{*d*} [*endo*-**3a**][PF₆]₂ in *d*₆.acetone, ¹H NMR (500 MHz, 298 K < T < 343 K), line shape analysis.

fragments on the rotational barrier of NMe₂ is rather limited, which explains why the diastereotopic Me groups in 2a, $[endo-4a]^+$, PF_6^- and [exo-5b] resonate as a single (coalesced) singlet within both ¹H and ¹³C NMR time scale. ΔG_{rot} values for III are about three times larger than those for II. Note here that the values of ΔG_{rot1} and ΔG_{rot2} are relatively similar in most cases. VT ¹H NMR experiments were carried out with 9.3 mM solutions of [endo-3a][PF₆]₂ in d₆-acetone and subsequent line-shape analysis of the dynamics of mutual exchange involving the methyls of the -NMe₂ substituent yielded the associated rotational barrier.¹⁸ Worthy to note, the exchange was found to be insensitive to variations of ionic strength (I) in acetone.§ Linear fitting ($R^2 = 0.99$) of the Eyring plot, *i.e.* $\ln(k_{rot}/T)$ vs. 1/T. (k_{rot} : rotational exchange rate constant), yielded a value for ΔG_{rot} (298.15 K) of +16.7(3) kcal mol⁻¹ $(\Delta H_{\rm rot} = +12.9(4) \text{ kcal mol}^{-1}, \Delta S_{\rm rot} = -12(1) \text{ cal mol}^{-1} \text{ K}^{-1}).$ This value of ΔG_{rot} was corroborated by further DFT calculations (including solvation) using the actual structure of the bis-cation $[endo-3a]^{2+}$ and its associated transition rotamers TS1-2_{3a} (Table 2). Information on the relative rehybridization of the nitrogen atom of the NMe2 group upon rotation can be inferred from the geometries of TS1-2_{3a} (Fig. S1, ESI[†]).

It is clear that the coordination of "Cp*Ir²⁺" to metallacycle 2a draws the electronic structure of the anilinyl fragment slightly closer to that of a η^5 -cyclohexadienyliminium limit form. The decrease of the wbi associated with the increase of $d_{\rm M}$ is consistent with a net shift to a *quasi* η^5 -coordination mode in III.¹⁹ The largest variation of *natural* (negative) charge at the nitrogen atom of the amino group relative to II, *i.e* $\Delta q(i)_{\rm N} = q_{\rm N}(i) - q_{\rm N}({\rm II}) (q_{\rm N}({\rm II}) = -0.398)$, is found for III ($\Delta q_{\rm N}$ (III) = 0.06), whereas only minor variations are computed for IV and V (0.008 and 0.004, respectively). Analysis of the *natural* charges borne by the π -bound metals provides a rationale for the observed facial selectivity in the formation of $[endo-3a]^{2+}$ and $[endo-4a]^{+}$. In both models III $(q_{\pi-\text{Ir}} = +0.58)$ and IV $(q_{\pi-\text{Ru}} = +0.29)$ the natural charge at the π -bound metal is significantly positive, which favors stabilizing interactions with the vicinal Ir-bound chlorido ligand ($q_{\rm Cl} \sim -0.44$). The strong charge density surrounding the latter atom is somewhat encapsulated within a "pocket" of low charge density, *i.e.* the rest of the molecule (cf. ESI[†]). For V, a large negative charge at the Cr atom ($q_{\pi-\text{Cr}} \sim -0.89$),

supplemented by largely negative CO oxygens, disqualifies the *endo* arrangement, which is in full agreement with earlier observations.¹⁷

In summary, this study shows that cationic and bis-cationic (*T*-4) iridacycles derived from 2-anilinylpyridines can be synthesized stereospecifically in high yield by reaction with the labile solvato complexes of "Cp*Ru⁺" and "Cp*Ir²⁺". Theoretical investigation points to the central role of Coulomb interactions in the preference given to the *endo* isomer of the cationic binuclear products. The key role of the NMe₂ group has also been outlined with the support of DFT. The rotational properties disclosed here indicate that the high rotational barrier results exclusively from electronic effects.

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Notes and references

‡ See ESI† for detailed crystallography.

§ Ionic strength *I* was adjusted by adding $[N(nBu)_4][PF_6]$ in three different VT NMR experiments, with I = 27 (no added salt), 37 (1 eq. of salt) and 121 mM (10 eq. of salt).

- 1 M. E. Gunay and C. J. Richards, *Organometallics*, 2009, 28, 5833–5836.
- 2 M. Albrecht, Chem. Rev., 2010, 110, 576-623.
- 3 S. Jautze, S. Diethelm, W. Frey and R. Peters, *Organometallics*, 2009, **28**, 2001–2004.
- 4 J.-P. Djukic, A. Hijazi, H. D. Flack and G. Bernardinelli, *Chem. Soc. Rev.*, 2008, **37**, 406–425.
- 5 S. Bonnet, M. Lutz, A. L. Spek, G. van Koten and R. J. M. Klein Gebbink, Organometallics, 2008, 27, 159–162.
- 6 A. Hijazi, J.-P. Djukic, L. Allouche, A. de Cian, M. Pfeffer, X.-F. Le Goff and L. Ricard, *Organometallics*, 2007, 26, 4180–4196.
- 7 C. Scheeren, F. Maasarani, A. Hijazi, J.-P. Djukic, M. Pfeffer, S. D. Zaric, X.-F. Le Goff and L. Ricard, *Organometallics*, 2007, 26, 3336–3345.
- 8 S. Bonnet, J. Li, M. A. Siegler, L. S. von Chrzanowski, A. L. Spek, G. van Koten and R. J. M. Klein Gebbink, *Chem.-Eur. J.*, 2009, 15, 3340–3343.
- 9 S. Bonnet, J. H. van Lenthe, M. A. Siegler, A. L. Spek, G. van Koten and R. J. M. Klein Gebbink, *Organometallics*, 2009, 28, 2325–2333.
- 10 S. Bonnet, M. Lutz, A. L. Spek, G. van Koten and R. J. M. Klein Gebbink, Organometallics, 2010, 29, 1157–1167.
- 11 J.-P. Djukic, L. Fetzer, A. Czysz, W. Iali, C. Sirlin and M. Pfeffer, Organometallics, 2010, 29, 1675–1679.
- 12 J. W. Kang, K. Moseley and P. M. Maitlis, J. Am. Chem. Soc., 1969, 91, 5970–5977.
- 13 D. L. Davies, O. Al-Duaij, J. Fawcett, M. Giardiello, S. T. Hilton and D. R. Russell, *Dalton Trans.*, 2003, 4132–4138.
- 14 M. D. Mbaye, B. Demerseman, J. L. Renaud, L. Toupet and C. Bruneau, Adv. Synth. Catal., 2004, 346, 835–841.
- 15 I. I. R. Salas, M. A. Paz-Sandoval and H. Nöth, Organometallics, 2002, 21, 4696–4710.
- 16 J. A. S. Howell, N. F. Ashford, D. T. Dixon, J. C. Kola, T. A. Albright and S. K. Kang, *Organometallics*, 1991, 10, 1852–1864.
- 17 J.-P. Djukic, C. Boulho, D. Sredojevic, C. Scheeren, S. Zaric, L. Ricard and M. Pfeffer, *Chem.-Eur. J.*, 2009, **15**, 10830–10842.
- 18 J. Sandström, Dynamic NMR spectroscopy, Academic Press, London, 1982.
- 19 A. D. Hunter, L. Shilliday, W. S. Furey and M. J. Zaworotko, Organometallics, 1992, 11, 1550–1560.