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Self-organisation in *P*-substituted guanidines leading to solution-state isomerisation†

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Different isomeric forms of the amidine unit have been identified in $Ph_2P(E)C\{NR'\}\{NHR'\}$ (E = S, Se; R′ = ^{i}Pr, Cy), using both solid- and solution-state techniques.

Amidines and guanidines, $RC\{NR'\}\{NHR'\}$, where R = alkyl/aryl or an amino group respectively, are known to adopt different isomeric and tautomeric forms dependent on the relative orientation of the imine bond and the position of the N*H* atom.[1] These fundamental structural differences have important consequences on the way in which these species interact with other molecules and, given their application as reagents and catalysts in organic transformations,[2] knowledge of the factors that determine the preference for these different forms is essential for understanding their activities and selectivities. Our main interest in this area originates from the effects that the different spatial arrangement of substituents have on the ability of these compounds to function as ligands,[3] where for example, constraining the substituents in the E_{anti} configuration has been shown to lead to stabilisation *via* intramolecular H-bonding.[4]

We recently reported the synthesis of the phospha(III)guanidine compounds, $Ph_2PC\{NR'\}\{NHR'\}$ [**1**, R′ = ^{i}Pr; **2**, R′ = Cy],[5] and structural analyses suggested that overlap between the phosphorus lone-pair and the sp^2-carbon was disfavoured, allowing these compounds to behave as phosphine donors. This combination of functionalities afforded flexible coordination behaviour,[6] with bonding to metals possible through either the phosphine or amidine units, or a combination of both. As an ambidentate ligand, bridging and chelating modes have been observed and examples of group 6 carbonyl compounds containing coordinated **2** as an *N*,*P*-chelate with a Z_{anti} configuration of substituents have been reported (Fig. 1a).[6] Considering that **1** and **2** have an E_{syn} arrangement in the solid-state, significant rearrangements within the amidine moiety must be occuring either prior to or as a result of coordination.

Conversion of **1** and **2** to the corresponding thio- and selenophosphorus(V) derivatives was achieved with elemental chalcogen, affording $Ph_2P(E)C\{NR'\}\{NHR'\}$† [E = S: **3**, R′ = ^{i}Pr; **4**, R′ = Cy. E = Se: **5**, R′ = ^{i}Pr; **6**, R′ = Cy].[7] Combustion and mass spectral analysis were consistent with the predicted formulation; however solution-state ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectra indicated the presence of a mixture of two species, described in detail for representative compound **6**.

The ^{1}H NMR spectrum of **6** (500 MHz, D$_8$-toluene, 293 K) contains two low field multiplets, a and b, corresponding to the *ortho*-C_6H_5 protons of two distinct species (Fig. 2). Saturation transfer experiments indicate that an equilibrium exists between these two forms (K_{eq} = 0.73 at 298 K). Further evidence for two species in solution is given by four resolved resonances (e–h) for the α-*H* of the Cy-groups, consistent with inequivalent *N*-substituents within the amidine unit of each form. The N*H* resonance at δ 5.42 (d) is present as an unresolved pseudo-triplet, exhibiting three-bond coupling of similar magnitude to both phosphorus and the α-C*H* of the N_{amine}-substituent. In contrast, no corresponding coupling is measurable in **1** and **2**, although in the Z_{anti} configuration at an 'M(CO)$_4$' fragment (Fig. 1a), $^3J_{PH}$ coupling is evident.[6] These data suggest that the extent of delocalization is influenced by the isomeric form of the amidine. Saturation transfer experiments indicate that d is in exchange with an additional pseudo-triplet at δ 6.96 (c), obscured by the aromatic resonances in Fig. 2.

Pairing of resonances c with h and d with e was established using selective decoupling, and the latter signal in each case is therefore assigned to the α-*H* of an N_{amine} Cy group. Selective irradiation of h resulted in signal enhancement for g, indicating the α-*H* of the corresponding N_{imine}-substituent; no such enhancement was observed between e and f due to more pronounced localization of the carbon-nitrogen single and double bonds. nOe experiments show that, upon irradiation of the *ortho*-phenyl protons a, the only enhancement observed corresponds to other aromatic resonances, while irradiation of b results in enhancement of both d (N*H*) and f (α-*H*, N_{imine}). This suggests free rotation about the P–CN$_2$ bond in one species and a 'locked' geometry in the other.

The appearance of two signals in the ^{31}P NMR spectrum (δ 36.0 and 24.3 in 1 : 1.3 ratio), each displaying selenium satellites ($^1J_{SeP}$ = −721, −753 Hz respectively), and two corresponding doublets in the ^{77}Se NMR spectrum (δ −223.6, −721 Hz; δ −310.9, −753 Hz) corroborate the presence of two species in solution. The proton coupled ^{77}Se experiments reveal the lower frequency resonance to have a further coupling of 6 Hz (Fig. 2 inset), which disappears on selective decoupling of proton c. The magnitude of this coupling is

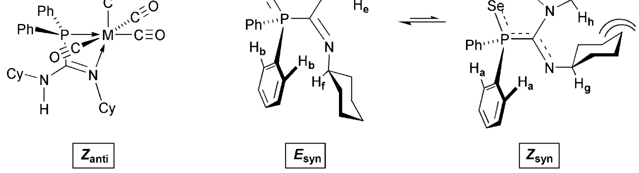

Fig. 1 (a) Z_{anti} configuration in group 6 carbonyl compounds of *P*-guanidines; (b) solution isomerisation in **6**.

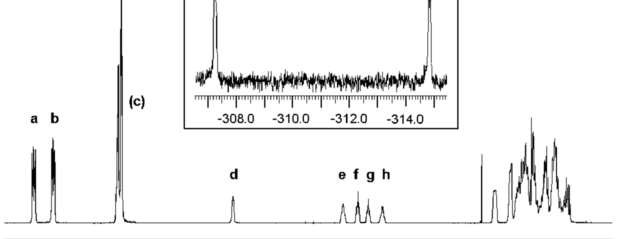

Fig. 2 ^{1}H NMR spectrum of **6** (500 MHz, D$_8$-toluene, 293 K) showing two isomeric forms in solution. Inset: High-field resonance of ^{77}Se NMR spectrum (^{1}H coupled) showing J_{SeH}.

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† Electronic supplementary information (ESI) available: Full synthetic data for compounds **3–6** and NMR and solution state IR spectra of **6**. See http://www.rsc.org/suppdata/cc/b4/b410041g/

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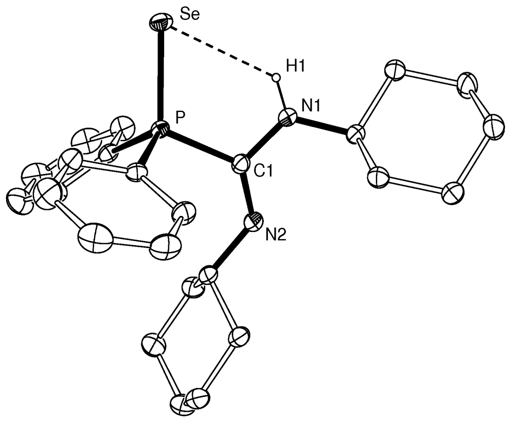

Fig. 3 Molecular structure of **6**. Selected bond lengths (Å) and angles (°): P–Se 2.1183(4), P–C(1) 1.8811(14), C(1)–N(1) 1.3602(18), C(1)–N(2) 1.2785(18); P–C(1)–N(1) 111.07(10), P–C(1)–N(2) 127.96(11), N(1)–C(1)–N(2) 120.95(13).

less than predicted for a direct Se–H bonding interaction (typical values:[8] $^{1}J_{\mathrm{SeH}} \sim 50$ Hz; $^{2}J_{\mathrm{SeH}}/^{3}J_{\mathrm{SeH}} \sim 10$–20 Hz) and provides evidence for the presence of a weak[9] Se···H hydrogen-bonding interaction with the amide proton. It is noted however that this interaction is evidently still strong enough to slow rotation about the P–C_{amidine} bond on the NMR timescale to generate the observed 'locked' conformation.

These data represent strong evidence for the existence of E_{syn} and Z_{syn} isomerisation of the amidine unit in solution (Fig. 1b). Variable temperature ^{1}H NMR experiments† show that below 248 K the ratio of E_{syn} : Z_{syn} isomers remains constant at 1.00 : 0.40 (average over 248 K–198 K). Upon warming above this temperature, the relative amount of the Z_{syn} form increases to afford a 1.00 : 0.73 ratio at 298 K. Van't Hoff analysis of the data between 248 K and 298 K gave a value for ΔH of 11.3 kJ mol^{-1} and ΔS of +38.2 J mol^{-1} K^{-1}.

The solution IR spectrum† of **6** ($CDCl_3$) reflects the presence of these two isomers, with a broad absorption [3262 cm^{-1}] assigned to ν(N–H···Se) and a sharp signal [3428 cm^{-1}] for the terminal ν(N–H). Compared with calculated [~2550 cm^{-1}],[10] and observed [2240–2320 cm^{-1}],[11] Se–H absorptions, the former value is too high to be considered as originating from a Se–H bond.

NMR data also suggest that the Z_{syn} configuration promotes redistribution of electron density in **6**, indicated by changes in the J_{PC} values. An unusually large $^{1}J_{\mathrm{PC}}$ coupling [123.4 Hz] is observed to the PCN_2, approximately three times the corresponding value in the E_{syn} isomer [141.3 ppm, 42.8 Hz] and the phospha(III)guanidines (32.0 Hz).[6] Also, in contrast to **1** and **2** where $^{3}J_{\mathrm{PC}}$ coupling to the α-CH of the N-substituents is only observed through the C=N bond, the methine carbons of both Cy-groups couple to phosphorus in **6**. Solution IR measurements indicate a sharp ν(CN) absorption [1618 cm^{-1}] with an additional absorption at ~1510 cm^{-1} (overlapping with solvent absorption). In comparison with the single absorption at 1590 cm^{-1} for **2**, these are assigned to the E_{syn} and Z_{syn} isomers respectively, where the latter red-shifted absorption is consistent with the postulated increase in electron delocalization.

Structural studies have previously been conducted on related selenophosphinylthioformamides;[12] however the absence of spectroscopic data prohibits correlation with the solution-state structures. The molecular structures‡ of **4** and **6** show that both compounds exist as monomers in the solid-state, based around a distorted tetrahedral phosphorus atoms (**6**, Fig. 3). The P=Se bond in **6** [2.1183(4) Å] is comparable with related organophosphorus(V)selenides.[13] The P–CN_2 bond length [**6**, 1.8811(14) Å] is similar to the corresponding value in the phospha(III)guanidine precursor [**2**, 1.878(2) Å], indicating no significant contribution from a phosphaalkene resonance form.

The ground state of **6** has an E_{syn} arrangement of the amidine substituents, with a Se = P–C(1) and N(1)–C(1)–N(2) twist angle of only 12°, and a short N*H*···Se distance [2.69 Å]. We suggest that this preferred orientation of the amidine unit is electrostatic in origin, probably due to a large contribution from the zwitterionic $P^{[+]}$–$Se^{[-]}$ resonance form. In this configuration, the barrier to isomerisation of the C=N bond is evidently lowered in solution, allowing formation of the sterically less favourable Z_{syn} isomer. This in turn forces the N*H* into even closer proximity to selenium, accounting for the observed J_{SeH} coupling.

Studies into the application of these compounds as ligands in coordination chemistry are ongoing in the group.

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Notes and references

‡ **4**: $C_{25}H_{33}N_2PS$, M = 424.56, T = 173(2) K, monoclinic, space group $P2_1/c$ (No. 14), a = 14.3934(2), b = 9.6078(2), c = 17.3407(3) Å, β = 100.495(1), U = 2357.91(7) Å^3, Z = 4, D_c = 1.20 Mg m^{-3}, μ (Mo Kα) = 0.22 mm^{-1}, independent reflections = 4118 [R_{int} = 0.065], R_1 [for 3539 reflections with $I > 2\sigma(I)$] = 0.035, wR_2 (all data) = 0.087. **6**: $C_{25}H_{33}N_2PSe$, M = 471.46, T = 223(2) K, triclinic, space group P_{i} (No. 2), a = 8.8687(1), b = 9.6892(1), c = 14.9910(2) Å, α = 82.172(1), β = 82.934(1), γ = 69.345(1)°, U = 1190.24(2) Å^3, Z = 2, D_c = 1.32 Mg m^{-3}, μ (Mo–Kα) = 1.66 mm^{-1}, independent reflections = 5599 [R_{int} = 0.030], R_1 [for 5129 reflections with $I > 2\sigma(I)$] = 0.025, w$R2$ (all data) = 0.059. CCDC numbers 244048 and 244049. See http://www.rsc.org/suppdata/cc/b4/b410041g/ for crystallographic data in .cif or other electronic format.

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