

N-benzoylimido complexes of palladium. Synthesis, structural characterisation and structure–reactivity relationship

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Benzoyl azides, ArC(O)N₃, **2**, (Ar = phenyl or substituted phenyl), react with [Pd₂Cl₂(dppm)₂], **1**, [dppm = bis(diphenylphosphino)methane] with the formation of novel [Pd₂Cl₂(μ-NC(O)Ar)(dppm)₂], **3**, benzoylnitrene complexes that were structurally characterised by multinuclear magnetic resonance and IR spectroscopy and, in several instances, by single crystal X-ray diffraction. As shown by crystallographic studies, the C₂P₄Pd₂ rings adopt extended twist–boat conformations with methylene groups bending towards the bridging benzoylimido moieties. X-ray diffraction studies have revealed the chiral nature of the imido complexes, the chiral element being the propeller-like C₂P₄Pd₂ ring. Structural data accumulated on complexes **3** such as short C–N distances (1.32 Å), elongated C=O bonds (1.30 Å) as well as the outstandingly high barrier to internal rotation around the N–C(O) linkage (88.3 kJ mol⁻¹) are in line with extensive ππ–ππ interaction between the bridging nitrogen and the carbonyl carbon atoms. Theoretical calculations indicate an electron shift from the dimer towards the apical nitrogen atom, which, in turn, facilitates the donation of electrons towards the carbonyl moiety. To elucidate the structure–reactivity relationship of benzoyl azides towards **1**, crystallographic and solution IR spectroscopic studies were carried out on a series of *para*-substituted benzoyl azides. The reaction obeys the Hammett equation. The large positive value of the reaction constant indicates that the azides act as electrophiles in the reaction studied. The enhanced reactivity of 2-nitrobenzoyl azide has been attributed to a decreased conjugation of the phenyl and carbonyl moieties in this reagent.

Introduction

The chemical literature reflects an unceasing interest in the chemical and structural properties of transition metal imido (nitrene) complexes.¹ The attractiveness of imido complexes can partly be attributed to the diversity of coordination modes of the imido moieties attached to metal centres.^{1c} Another reason for initiating studies on nitrene complexes has been the expectation that such species may emerge as intermediates in catalytic transformations.² Nowadays, the observation that imido complexes possess remarkable catalytic activity expands the scope of both the synthetic and the catalytic investigations carried out with coordination compounds incorporating nitrene species.³

The relatively easy access to a wide range of organic azides and their readiness to liberate dinitrogen in the coordination sphere of metal ions have made these compounds promising substrates for the preparation of imido complexes. A summary of the earlier results has appeared⁴ and, utilising the reactivity of organic azides toward metal complexes, numerous novel nitrene adducts have been prepared since then.⁵ In the majority of publications, aryl azides and, to a lesser extent, arenosulfonyl azides were employed as reagents. Aryl azides, however, have played so far only an episodic role. Apart from the early observations of Kaska and coworkers,⁶ the thermal reaction of aroyl azides with coordination compounds did not result in the formation of isolable nitrene complexes. Collman and coworkers demonstrated that the reaction of iridium complexes with aroyl azides gives dinitrogen complexes in protic solvents while the same reaction results in acyl isocyanate complexes in the absence of acidic hydrogen atoms.⁷ A similar reaction course was suggested for the interaction of a rhodium dimer with benzoyl azide.⁸ The formation of acyl isocyanate complexes were also noted in the reaction of monomeric Ru(0) complexes with benzoyl azide.⁹ On the contrary, the reaction of

platinum hydrides with benzoyl azide was reported to yield air stable *N*-benzoylamido complexes rather than imides.¹⁰ *N*-benzoylnitrene adducts have shown up sometimes, however, although in low yield. The photochemical decomposition of benzoyl azide in the presence of [CpMo(CO)₃CH₃] produced traces (2 %) of a dimolybdenum complex incorporating a bridging *N*-benzoylimido moiety.^{11a} Rather unexpectedly, the interaction of the tungsten complex [WCl₂(NC₆H₃Pr^{*i*}_{2-2,6})(PMe₃)₃] with unpurified *p*-toluonitrile gave reproducibly small amounts of the mononuclear benzoylnitrene complex [WCl₂(NC₆H₃Pr^{*i*}_{2-2,6})(NC(O)C₆H₄Me-4)(OPMe₃)(PMe₃)].¹² It might be due to the inefficiency of synthetic procedures that structural data related to benzoylimido adducts are rare and there seems to be no systematic studies aimed at their synthesis and characterisation.

In the course of our search for viable routes to nitrene complexes of palladium, we have observed that the interaction of the dimer [Pd₂Cl₂(dppm)₂], **1**, with arenosulfonyl azides affords dinuclear nitrene adducts in high yield.¹³ Moreover, this reaction has allowed the isolation of azide complexes if the sulfonyl azide carries at least one *ortho*-substituent.^{13,14} The structure–reactivity relationship was also investigated for a series of *para*-substituted benzenesulfonyl azides.¹⁵

The scarcity of structural data of *N*-aroylimido complexes, the lack of systematic investigations on the interaction of aroyl azides with metal complexes and also the special attention devoted to the imido complexes of the late transition metals^{1a,b,16} have prompted us to extend our studies to the interaction of the dimeric palladium complex **1** with benzoyl azides. In order to facilitate the interpretation of our experimental findings, we performed density functional calculations for a series of benzoyl azides as well as for some of the *N*-benzoylimido complexes. The results of our theoretical studies are also reported here. An extensive study on the crystal structures of the benzoyl azide reagents has been published recently.¹⁷

Experimental

The work outlined below required benzoyl azides that are stable as isolated compounds and can be purified efficiently for kinetic and IR investigations. It was also our aim that the substituents on the phenyl ring cover a wide range of Hammett's σ constants. An overview of literature data¹⁸ allowed a choice of a series of azides satisfying our requirements. Although we did not experience any dangerous situations with the compounds selected, one must keep in mind that working with isolated benzoyl azides can be hazardous especially when *ortho* substituents are present.¹⁹

Experimental methods

NMR spectra were recorded in CDCl_3 or CD_2Cl_2 solutions at ambient temperature on Varian Unity Inova and Varian Unity 300 spectrometers. The resonance frequencies were 400 and 300 MHz for ^1H , 101 and 75.4 MHz for ^{13}C , 121.4 MHz for ^{31}P and 282.2 MHz for ^{19}F . Chemical shifts are reported with reference to TMS (^1H , ^{13}C), 85% H_3PO_4 (^{31}P) and CFCl_3 (^{19}F). VT NMR experiments were carried out in $\text{DMSO}-d_6$ solutions. Infrared spectra of the benzoyl azides were recorded in 0.02–0.03 M CCl_4 solutions using a Nicolet Magna 750 FT IR spectrometer. IR spectra of complexes **3** were measured in CH_2Cl_2 solutions on Nicolet Avatar 320 FT IR equipment ($l = 0.0127$ cm, resolution 4 cm^{-1}). Because of the poor solubility of the complexes (1.2–3.0 mM), 2048 scans were accumulated to achieve a good S/N ratio. UV-vis spectra were taken on a HP 8453 diode array spectrophotometer using CH_2Cl_2 as solvent. Mass spectra were obtained on samples suspended in *m*-nitrobenzyl alcohol using a VG-ZAB-2SEQ spectrometer. Elemental analyses were carried out on vacuum dried samples (methanol reflux, *ca.* 0.1 Torr).

X-ray diffraction

Intensity data were collected on an Enraf-Nonius CAD4 diffractometer at 293(2) K (graphite monochromator; Mo-K α radiation, $\lambda = 0.71073\text{ \AA}$ [**3b**, **3f**] and Cu-K α radiation, $\lambda = 1.54184\text{ \AA}$ [**3c**, **3e**]) using $\omega/2\theta$ scans. Empirical absorption corrections²⁰ (psi-scans) were applied in all cases. The structures were solved by direct methods²¹ and Fourier techniques and refined by anisotropic least-squares²² on F^2 for all non-hydrogen atoms. Hydrogen atomic positions were calculated from assumed geometries and were included in structure factor calculations but were not refined. The structures of **3b–c** were also determined in space groups $P4_3/P4_1$. The $\text{C}(\text{O})\text{C}_6\text{H}_4\text{CN}$ moieties turned out to be disordered. The site occupation factor for this moiety in **3b** refined to 0.5 was within 2σ . Atomic coordinates for all non-hydrogen atoms indicated the presence of an additional symmetry element, a two-fold axis passing through the nitrene nitrogen and the carbonyl carbon atoms (space group $P4_32_12$, with half a molecule in the asymmetric unit). In order to test which space group gives a more adequate description of the crystal structure, the refinement in both space groups was repeated starting with isotropic atoms. Every tenth reflections (1997 in $P4_3$ and 999 in $P4_32_12$) were put aside for $R(\text{free})$ testing. The $R(\text{free})$ values were always lower for the higher symmetry model (the final $R(\text{free})$ values were 0.0604 for 1119 $F_o > 4\sigma(F_o)$ and 0.1266 for all data for $P4_3$ and 0.0476 for 573 $F_o > 4\sigma(F_o)$ and 0.0925 for all data for $P4_32_12$). A similar procedure was followed for **3c** verifying that the space group was indeed $P4_32_12$. This type of disorder is not unprecedented at all,²³ and analogous cases are described^{23g} for two A-frame complexes of palladium (space group $P4_32_12$). All phenyl rings were treated as regular hexagons ($\text{C–C} = 1.390\text{ \AA}$) for **3c** because further positional disorder was detected. Neutral atomic scattering factors and anomalous scattering factors were taken from ref. 24.

CCDC reference numbers: 232756–232759.

See <http://www.rsc.org/suppdata/dt/b4/b403200d/> for crystallographic data in CIF or other electronic format.

Kinetic studies

All kinetic experiments were carried out in dichloromethane at 25 °C. The rate constants k ($\text{M}^{-1}\text{ s}^{-1}$) were determined for the most reactive azides, **2a**, **2b** and **2h**. In these kinetic runs, the reaction of $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$, **1**, with benzoyl azides was monitored by recording the UV-vis spectra as a function of time on a Hewlett–Packard 8453 diode-array spectrophotometer (method 1). In the case of the less reactive azides, determination of the ratio of rate constants for a selected pair of azides was based on experiments in which **1** was allowed to react simultaneously with two benzoyl azides added in the same (25-fold) molar excess to the reaction mixture. Integration of selected regions of the ^1H NMR spectra of the isolated products allowed us to calculate the molar ratio of the imido complexes formed that equals the ratio of the rate constants as well (method 2).²⁵ A typical experiment was carried out as follows: to a solution of 20.6 mg (0.0196 mmol) of $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$ in 0.4 ml of dichloromethane was added a solution of 43.2 mg (0.225 mmol) of 4-nitrobenzoyl azide and 43.0 mg (0.224 mmol) of 2-nitrobenzoyl azide in 0.6 ml of dichloromethane. The capped vial was kept for 30 min in a water bath thermostated at $25 \pm 0.1\text{ }^\circ\text{C}$. TLC indicated full conversion of the dimer. *n*-Hexane (6 ml) was added to the reaction mixture and the solvents were removed under vacuum. The yellow precipitate was suspended in hexane, transferred onto a glass filter and washed repeatedly with hexanes to remove the unreacted azides. Integration of the resonances emerging at 3.95 and 3.21 ppm in the ^1H NMR spectrum allowed the calculation of the molar ratio of the imido complexes formed from the two competing azides. Because of their low solubilities, special care should be taken with mixtures containing imido complexes derived from 4-fluorobenzoyl azide or benzoyl azide to ensure complete dissolution of the sample.

Computational details

The structure of the investigated species has been optimized at the B3LYP/SDDP level of density functional theory, where B3LYP refers to the hybrid-type exchange-correlation functional,^{26–28} and SDDP denotes a basis set that involves the Stuttgart–Dresden quasi-relativistic ECP basis set for Pd²⁹ and the Dunning/Huzinaga DZP all electron basis set for the lighter atoms.^{30–32} The harmonic vibrational frequencies have been obtained from analytical second derivatives at the same level of theory.

A simplified structural model was used to represent the $[\text{Pd}_2\text{Cl}_2(\mu\text{-NC}(\text{O})\text{Ar})(\text{dppm})_2]$ complexes, where the phenyl groups of the dppm ligands were replaced by hydrogens. As a consequence of the $\text{dppm} \rightarrow \text{H}_2\text{PCH}_2\text{PH}_2$ approximation, which was introduced to keep the computations within reasonable bounds, the steric interactions between the bulky dppm ligands and the aryl group of the benzoylimido moieties are neglected, however, we expect that the electronic effects governing the structure of the $\text{Pd}_2(\mu\text{-NC}(\text{O})\text{Ar})$ units are described reasonably well with the $[\text{Pd}_2\text{Cl}_2(\mu\text{-NC}(\text{O})\text{Ar})(\text{H}_2\text{PCH}_2\text{PH}_2)_2]$ model. All our calculations were performed using the Gaussian 98 program package.³³

Preparations

$[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$ was prepared according to an established procedure.³⁴ The known benzoyl azides **2a–h** were synthesised by literature methods.³⁵ Purification of the crude products was accomplished either by column chromatography or by sublimation at *ca.* 0.1 Torr. To our knowledge, compound **2i** is new¹⁸ and was obtained *via* the following procedure. A solution of 0.44 g (6.8 mmol) of NaN_3 in 4 ml of water was added drop-

Table 1 Selected spectroscopic data of the imido complexes [Pd₂Cl₂(μ-NC(O)Ar)(dppm)₂], **3a-i**

	¹ H NMR	³¹ P NMR ^b	¹³ C NMR ^b		IR data ^c	
	Aliphatic H atoms δ _H /ppm (J _{HH} ; J _{HP})/Hz	δ _P /ppm	CO group δ _C /ppm	Other aliphatic carbon atoms δ _C /ppm	ν(CO)/cm ⁻¹	ν(CN)/cm ⁻¹
3a	2.56 (12.9; 3.4) ^a	10.8	171.2		^f	^g
4-NO ₂	3.21 (12.9; 5.3)	12.7				
3b	2.59(13.0; 3.4) ^b	10.9	171.4	119.3 (s, CN)	1505	1357
4-CN	3.15 (13.0; 5.4)	12.7				
3c	2.56 (12.9; 3.4) ^b	11.1	172.5		1496	1356
4-Br	3.19 (12.9; 5.5)	13.0				
3d	2.56 (12.9; 3.3) ^b	10.1	^c		1494	1362
4-F	3.23 (12.9; 5.5)	11.9				
3e	2.56 (12.8; 3.3) ^b	11.3	^c		1500, 1489	1361
4-H	3.26 (12.8; 5.5)	12.9				
3f	2.56 (12.8; 3.3) ^b	11.5	173.4	55.4 (s, CH ₃ O)	1488	1362, 1352
4-CH ₃ O	3.24 (12.9; 5.5)	13.3				
	3.56 (3H, s)					
3g	2.48 (13.0; 3.4) ^b	11.8	174.3	40.4 (s, (CH ₃) ₂ N)	1482	1357
4-(CH ₃) ₂ N	3.28 (13.0; 5.3)	13.3				
	2.75 (6H, s)					
3h	2.66 (12.9; 3.3) ^a	10.5	167.4		(1499) ^f	(1351) ^g
2-NO ₂	3.95 (12.9; 5.5)	11.2				
3i	2.54 (12.8; 3.3) ^a	10.0	169.9	123.1 (qua, CF ₃ , J _{CF} = 273 Hz) ^d	1521	(1321)
3,5-CF ₃	3.24 (12.8; 5.4)	12.0				

^a CDCl₃. ^b CD₂Cl₂. ^c Not determined. ^d ¹⁹F NMR: 65.2 ppm (s). ^e In CH₂Cl₂ solutions. ^f Masked by ν_{as}(NO₂) band. ^g Masked by ν_s(NO₂) band; m—multiplet; qua—quartet; s—singlet.

by-drop to 1.52 g (5.5 mmol) of 3,5-bis(trifluoromethyl)benzoyl chloride dissolved in 12 ml of acetone at 0 °C. After 30 min of stirring at this temperature, 30 ml of water was added and the reaction mixture was extracted with CH₂Cl₂ (3 × 15 ml). Drying over anhydrous MgSO₄ and evaporation under vacuum afforded a slightly yellow oil that was chromatographed on a silica gel column using hexane, and mixtures of dichloromethane and hexane as eluents. Yield after purification: 0.9 g (58%). NMR data (CDCl₃), ¹H NMR: 8.47 (2H), 8.09 (1H); ¹³C NMR: 170.2 (CO), 132.9, 132.8 (qua, J_{CF} = 34 Hz), 129.6, 127.6, 122.9 (CF₃, qua, J_{CF} = 274 Hz); IR data (CCl₄, cm⁻¹): 2217 and 2147 (ν_{as}(N₃)), 1706 (ν(CO)), 1280, 1221, 1187, 1149.

Preparation of the imido complexes 3a-i. The following recipe describes a typical synthesis. 210 mg (0.93 mmol) of 4-BrC₆H₄-C(O)N₃ dissolved in 2 ml CH₂Cl₂ was added to a solution of 158 mg (0.15 mmol) of [Pd₂Cl₂(dppm)₂] in 4 ml of CH₂Cl₂. The solution was kept in the dark for 24 h. TLC (Merck Kieselgel 60 F₂₅₄, dichloromethane/ethyl acetate 1:1) indicated full conversion of the dimer. Adding methanol completed precipitation of the product, which was collected on a glass filter and washed repeatedly with small portions of hexane and ethyl ether. The isolated yellow crystals (0.17 g, 91%) were dissolved in CH₂Cl₂ and reprecipitated with hexanes to remove traces of unreacted azide. Other *N*-benzoylimido complexes were prepared analogously but the time necessary to complete the reaction was strongly influenced by the substituent of the benzoyl azide. Approximate reaction times, yields and elemental analytical data: **3a** (4 h, 94 %), Found: C, 56.2; H, 3.8; N, 2.4. C₅₉H₅₄Cl₂N₂O₃P₄Pd₂ requires C, 56.27; H, 3.98; N, 2.30%. **3b** (6 h, 98 %), Found: C, 57.9; H, 4.1; N, 2.4. C₅₈H₄₈Cl₂N₂O₄Pd₂ requires C, 58.21; H, 4.04; N, 2.34%. **3c** (20 h, 91 %), Found: C, 54.7; H, 3.7; N, 1.2. C₅₇H₄₈BrCl₂NOP₄Pd₂ requires C, 54.75; H, 3.87; N, 1.12%. **3d** (2 d, 88 %), Found: C, 57.3; H, 4.1; N, 1.1. C₅₉H₄₈Cl₂FNOP₄Pd₂ requires C, 57.55; H, 4.07; N, 1.18%. **3e** (4 d, 88 %), Found: C, 57.8; H, 4.3; N, 1.2. C₅₇H₄₉Cl₂NOP₄Pd₂·H₂O requires C, 57.55; H, 4.32; N, 1.18%. FAB-MS: *m/z* (M⁺) 1171.1; C₅₇H₄₉Cl₂NOP₄Pd₂ requires 1171.0. **3f** (5 d, 70 %), Found: C, 57.8; H, 4.2; N, 1.2. C₅₈H₅₁Cl₂NO₂P₄Pd₂ requires C, 57.97; H, 4.28; N, 1.17%. **3g** (10 d, 60 %), Found: C, 56.5; H, 4.2; N, 2.1. C₅₉H₅₄Cl₂N₂O₄Pd₂·1/2CH₂Cl₂ requires C, 56.84; H, 4.41; N, 2.23%. FAB-MS: *m/z* (M⁺) 1214.4;

C₅₉H₅₄Cl₂N₂O₄Pd₂ requires 1214.1. **3h** (1 h, 96 %), Found: C, 56.3; H, 4.0; N, 2.3. C₅₇H₄₈Cl₂N₂O₃P₄Pd₂ requires C, 56.27; H, 3.98; N, 2.30%. **3i** (30 h, 69 %), Found: C, 51.7; H, 3.5; N, 1.0. C₅₉H₄₇Cl₂F₆NOP₄Pd₂·CH₂Cl₂ requires C, 51.75; H, 3.55; N, 1.01%. FAB-MS: *m/z* (M⁺) 1307.1; C₅₉H₄₇Cl₂F₆NOP₄Pd₂ requires 1307.0.

Results and discussion

Benzoyl azides ArC(O)N₃, **2**, react with the dimer [Pd₂Cl₂(dppm)₂], **1**, affording novel *N*-benzoylimido complexes, **3** (eqn. (1)) (Ar = **3a**—4-NO₂C₆H₄, **3b**—4-CNC₆H₄, **3c**—4-BrC₆H₄, **3d**—4-FC₆H₄, **3e**—C₆H₅, **3f**—4-CH₃OC₆H₄, **3g**—4-(CH₃)₂-NC₆H₄, **3h**—2-NO₂C₆H₄, **3i**—3,5-(CF₃)₂C₆H₃).



Reaction (1) takes place smoothly at ambient temperature (20–25 °C) in the dark. Benzoyl azides are known to rearrange thermally to amines or carbamic acid derivatives with the involvement of free nitrene intermediates. Although a small amount of *N,N'*-bis(2-nitrophenyl)urea was observed in the reaction of **1** with **2h**, the rest of the azides did not produce noticeable amounts of Curtius-type by-products and the unreacted azides could be recovered and identified (IR, TLC) at the end of the reaction. The good selectivity for the imido adducts allows the conclusion that reaction (1) is not associated with the appearance of free nitrene species. Most nitrenes are stated to be extremely reactive and one cannot expect them to react particularly selectively with a single constituent of a reaction mixture. Although a dimolybdenum benzoylimido complex was generated under photolytic conditions with the potential participation of free nitrene intermediates,^{11a} in reaction (1) decomposition of the azides certainly takes place in the coordination sphere of the palladium ions.

Solution characterisation of complexes 3

The ¹H NMR data reported in Table 1 readily prove that complexes possessing the expected A-frame structures are formed. The doublet/quintet splitting pattern of the methylene hydrogen atoms supports the apical position of the imido

fragments. The range of the chemical shifts and the extent of the J_{HH} and J_{HP} coupling constants correspond to those observed with structurally closely related complexes.^{13,36} It seems worth mentioning that the high and low frequency resonances of the methylene hydrogens show up in narrow ranges of 2.48–2.66 and 3.15–3.28 ppm, respectively, with the only exception of the high frequency multiplet of the 2-nitro-derivative, **3h**, that appears at 3.95 ppm. The DFT calculations carried out for the $[\text{Pd}_2\text{Cl}_2(\mu\text{-NC}(\text{O})\text{C}_6\text{H}_4\text{NO}_2\text{-2})\text{(H}_2\text{PCH}_2\text{PH}_2)_2]$ model compound reveals the existence of an appreciable intramolecular interaction between the nitro group and the axial methylene hydrogens ($d(\text{O} \cdots \text{H}) = 2.26 \text{ \AA}$, see Fig. 1). As the benzoyl phenyl group twists about the $\text{C}_{\text{ipso}}\text{-C}(\text{O})$ bond, the *ortho* nitro group can significantly alter the environment of the axial methylene hydrogen atoms compared to that experienced in the case of the *para*- and *meta*-substituted derivatives. We believe that it is the influence of the *ortho* nitro substituent that is reflected by the remarkable value of this chemical shift. A similar hydrogen bond for the *para*-substituted derivative is not feasible.

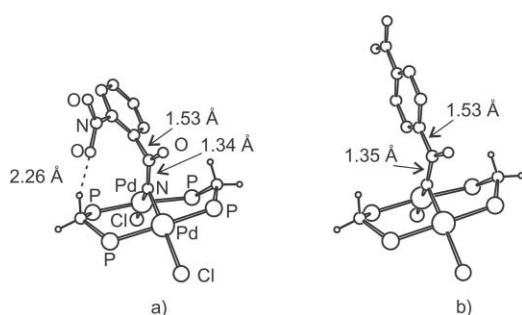


Fig. 1 Calculated structures for 2-NO₂- (a) and 4-NO₂-substituted (b) $[\text{Pd}_2\text{Cl}_2(\mu\text{-NC}(\text{O})\text{Ar})(\text{H}_2\text{PCH}_2\text{PH}_2)_2]$ model complexes (H atoms belonging to the aryl and PH_2 groups have been omitted for clarity).

The analysis of the aromatic region of the ¹H and ¹³C NMR spectra revealed four different sets of dppm phenyl groups. The non-equivalence of the phenyl groups located on the same side of the $\text{C}_2\text{P}_4\text{Pd}_2$ ring indicates a reduced symmetry compared to the previously described sulfonylnitrene complexes¹³ and is supported by the ³¹P{¹H} NMR spectra which invariably show up as AA'BB'-type multiplets for all the imido complexes **3**. This splitting pattern is typical for unsymmetrical A-frame complexes and is generally induced by an asymmetric dis-

position of the apical moiety with respect to the P nuclei. As proved by structural investigations (see below), the non-equivalence of the P nuclei can be attributed to hindered rotation about the N–C(O) bonds. This behaviour of the benzoylimido complexes is characteristically different from that of the sulfonylnitrene congeners which all but the sterically overcrowded $[\text{Pd}_2\text{Cl}_2(\mu\text{-NSO}_2\text{Tip})(\text{dppm})_2]$ adduct displayed a sharp singlet in their solution ³¹P spectra thereby supporting free rotation around the N–S axes (Tip = 2,4,6-tris(isopropyl)phenyl group).^{13,14} No hindered rotation was observed to emerge in the peripheral regions of molecules **3**. Resonances ascribed to the hydrogen and carbon atoms residing in the *ortho* positions of the dppm phenyl groups support free rotation around the P–C_{aryl} bonds. Likewise, there is no sign of a barrier to internal rotation for the phenyl ring of the *para*- and *meta*-substituted benzoyl fragments at ambient temperature.

Crystallographic description of complexes **3**

In order to shed light on the fine structural details of the imido complexes, X-ray diffraction studies were carried out on single crystals of **3b–c** and **3e–f**. The molecular structures are shown in Figs. 2–3. Crystal data and data collection parameters are summarised in Table 2. Selected bond lengths and angles are presented in Table 3.

The crystal structures of **3b–c** and **3e–f** are composed of discrete molecules that all crystallise in chiral space groups. The comparison of the enantiomorphous **3b–c** and **3e–f** reveals the chiral nature of these complexes. The chiral element is the propeller-like $\text{C}_2\text{P}_4\text{Pd}_2$ ring. A search of the Cambridge Crystallographic Database³⁷ for $[\text{M}_2\text{Cl}_2(\mu\text{-X})(\text{dppm})_2]$, (M = Pt, Pd, X = any atom or group) analogues crystallising in tetragonal space groups retrieved 16 hits²³ (7 $P4_1$; 6 $P4_3$; 2 $P4_12_12$, 1 $P4_32_12$) showing that the specimens subjected to investigation were selected randomly from spontaneously resolved crystal samples.

The palladium centres are bridged by two mutually *trans* dppm ligands and by the imido nitrogen atoms, which, in turn, are *trans* to the chloro ligands. In general, these molecules can be described as typical A-frame structures in which the methylene carbon atoms, as expected, are bent toward the apical nitrogen atoms. This arrangement lends an extended boat conformation to the eight-membered $\text{C}_2\text{P}_4\text{Pd}_2$ rings. The Pd–P distances (2.303–2.342 Å) and the Pd–Cl bond lengths (2.336–2.350 Å) lie in the expected ranges and are essentially the same as those observed for the sulfonylnitrene complexes.¹³

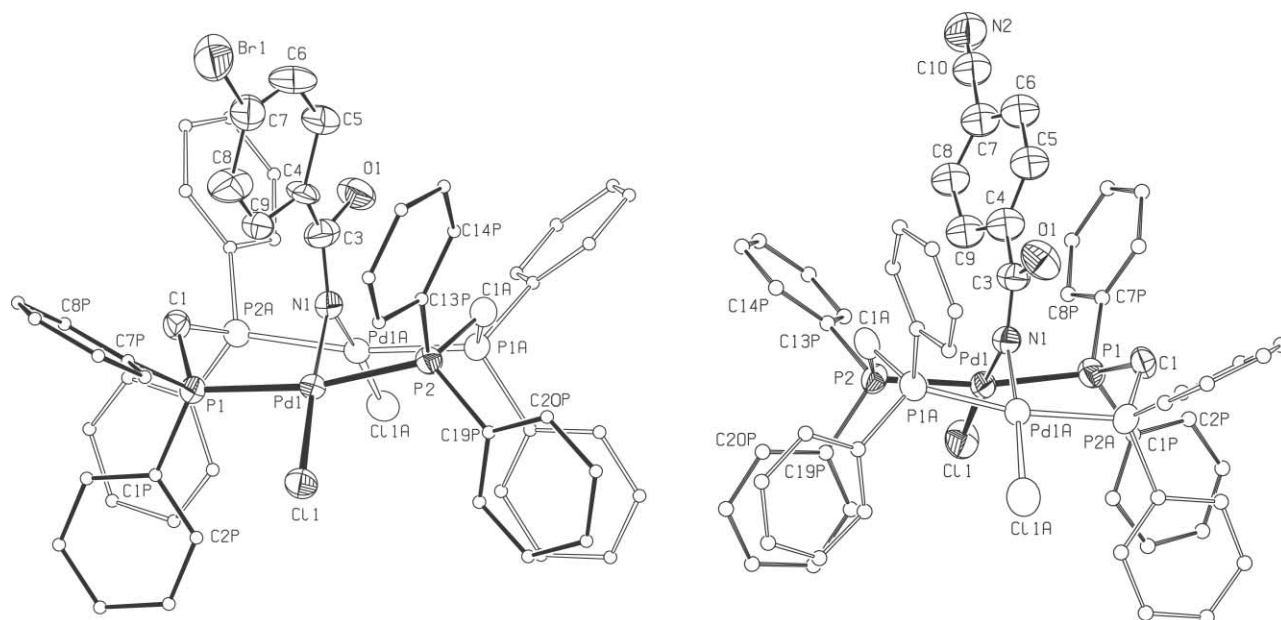
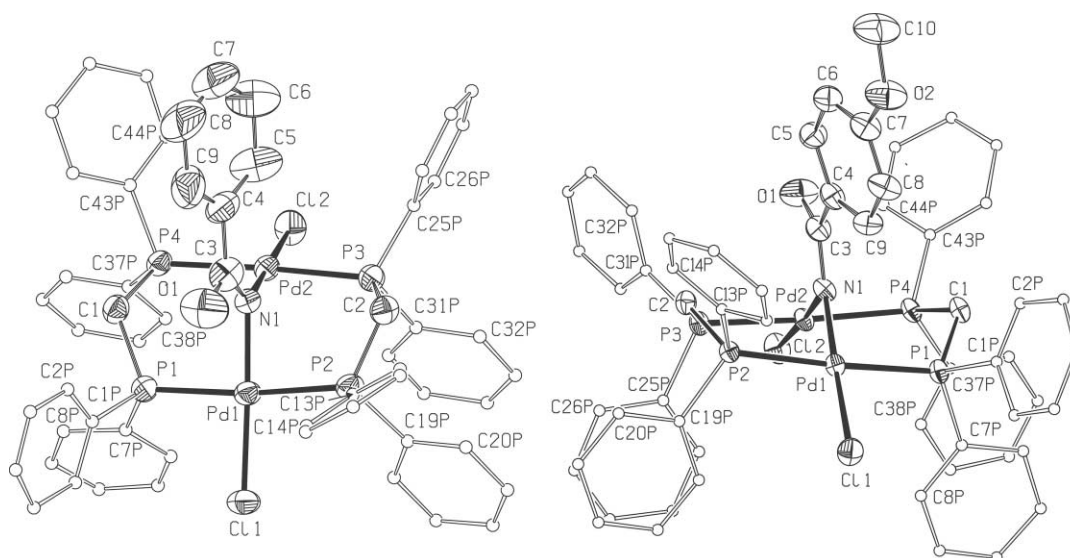


Fig. 2 The molecular structures of **3c** (left) and **3b**. Only one disordered fragment is shown. Hydrogen atoms are omitted for clarity.

Table 2 Crystal data, data collection and refinement parameters of *N*-benzoylnitrene complexes **3b–c** and **3e–f**

	3b	3c	3e	3f
Empirical formula	C ₅₈ H ₅₀ Cl ₂ N ₂ OP ₄ Pd ₂	C ₅₇ H ₄₈ BrCl ₂ NOP ₄ Pd ₂	C ₅₇ H ₄₉ Cl ₂ NOP ₄ Pd ₂	C ₅₈ H ₅₁ Cl ₂ NO ₂ P ₄ Pd ₂
Formula weight	1198.58	1250.45	1171.55	1201.58
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	<i>P</i> 4 ₃ 2 ₁ 2	<i>P</i> 4 ₃ 2 ₁ 2	<i>P</i> 4 ₁	<i>P</i> 4 ₃
Unit cell dimensions/Å	<i>a</i> = 15.011(7) <i>c</i> = 25.622(5)	<i>a</i> = 15.079(1) <i>c</i> = 25.970(3)	<i>a</i> = 21.247(3) <i>c</i> = 14.214(2)	<i>a</i> = 21.224(5) <i>c</i> = 14.230(2)
Volume/Å ³	5773(4)	5905.0(9)	6416.7(13)	6410(2)
<i>Z</i>	4	4	4	4
Density (calculated)/Mg m ⁻³	1.379	1.407	1.213	1.245
Absorption coefficient, μ/mm ⁻¹	0.865	7.846	6.485	0.780
<i>F</i> (000)	2424	2504	2368	2432
Crystal size/mm	0.50 × 0.45 × 0.25	0.25 × 0.20 × 0.12	0.25 × 0.10 × 0.10	0.40 × 0.16 × 0.16
Maximum/minimum transmission	1.0000/0.8656	1.0000/0.6526	1.0000/0.8267	1.0000/0.9938
<i>θ</i> -range for data collection/°	2.74–31.98	4.48–75.49	2.94–75.04	2.58–31.97
Reflections collected	22041	13245	14586	24367
Decay (%)	21%	2%	2%	6%
Independent reflections/ <i>R</i> (int)	9952/0.0731	6031/0.0888	12907/0.0290	22018/0.0178
Reflections <i>I</i> > 2σ(<i>I</i>)	5652	5118	8537	12729
Data/parameters	9952/ 356	6031/ 284	12907/ 607	22018/ 623
Goodness-of-fit on <i>F</i> ²	0.908	1.041	0.912	0.903
Absolute structure parameter	−0.01(3)	0.00(2)	−0.02(1)	−0.07(2)
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 0.0440 <i>wR</i> 2 0.0898	<i>R</i> 1 0.0610 <i>wR</i> 2 0.1501	<i>R</i> 1 0.0513 <i>wR</i> 2 0.1079	<i>R</i> 1 0.0542 <i>wR</i> 2 0.1176
<i>R</i> indices (all data)	<i>R</i> 1 0.0926 <i>wR</i> 2 0.1036	<i>R</i> 1 0.0690 <i>wR</i> 2 0.1564	<i>R</i> 1 0.0933 <i>wR</i> 2 0.1211	<i>R</i> 1 0.1150 <i>wR</i> 2 0.1318
Largest diff. peak/hole/e Å ⁻³	0.470/−0.949	1.330/−1.147	0.402/−0.763	1.237/−1.552

**Fig. 3** The molecular structures of **3e** (left) and **3f**. Hydrogen atoms are omitted for clarity.

The angles formed by the neighbouring ligands of the metal centres (85–95°) reflect a slight distortion from the square planar configuration around the palladium atoms. Accordingly, the P–Pd–P and N–Pd–Cl axes are slightly bent, the deviation from the ideal 180° is more pronounced in the former case. The Pd ⋯ Pd distances cover the range of 3.127(1)–3.247(1) Å and are consistent with the lack of metal–metal bonding interaction. These values, however, are noticeably shorter than those found in the sulfonylnitrene congeners, in which the bridging nitrogen atoms span Pd ⋯ Pd distances of 3.231(1)–3.350(1) Å. According to a recent crystallographic study, the palladium–palladium bond length in the parent [Pd₂Cl₂(dppm)₂], **1**, is 2.661(1) Å.³⁸ The increase of the Pd ⋯ Pd separation by 0.5–0.6 Å is in conformity with the structural changes observed at the formation of other A-frames incorporating one-membered apical bridges.³⁶ The bridging imido nitrogen atoms reside symmetrically between the palladium centres. The Pd–N bond lengths do not seem to be influenced by the electron withdrawing or electron-donating nature of the substituent attached to the benzoyl group and fall into the narrow range of

1.972(5)–2.001(4) Å. The mean value of the corresponding bond lengths is slightly longer in the sulfonylnitrene adducts (*d*(Pd–N,av) = 2.015 Å)

The most remarkable structural features of the benzoylnitrene complexes are associated with the imido moiety. The short N(1)–C(3) and the long O(1)–C(3) bond distances are common properties of the compounds **3b–c** and **3e–f** and suggest electron donation from the bridging imido nitrogen atom towards the carbonyl group. The multiple-bond nature of the N–C(O) bonds is substantiated by the N(1)–C(3) distances of about 1.32 Å. For comparison, C(sp³)–N and C(sp²)–N bond lengths have mean values of 1.47 and 1.38 Å, while C=N double bonds are typically 1.28 Å long.³⁹ Further supporting evidence for the strengthening of the N–C bonds in the imido complexes comes from the inspection of the data presented in Table 4. As shown in line 3, the respective bond lengths, C(7)–N(1), in the parent azides are by far longer (1.41–1.42 Å) and correspond rather to a carbon–nitrogen single bond.

As expected, the shrinkage of the N–C bonds is accompanied by the elongation of the O(1)–C(3) distances. Unfortunately,

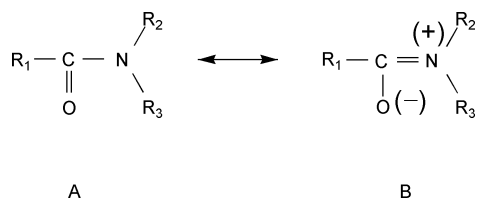
Table 3 Selected bond lengths and angles of the structurally characterised *N*-benzoylimido complexes **3b–c** and **3e–f**

	3b	3c	3e	3f
Pd(1)···Pd(2)	3.127(1)	3.151(1)	3.247(1)	3.246(1)
Pd(1)–N(1)	1.988(3)	1.972(5)	1.986(6)	1.999(4)
Pd(2)–N(1)			1.994(5)	2.001(4)
C(3)–N(1)	1.321(6)	1.310(7)	1.296(9)	1.319(7)
C(3)–O(1)	1.319(4)	1.321(1)	1.31(1)	1.295(7)
C(3)–C(4)	1.45(2)	1.416(7)	1.47(1)	1.479(7)
Pd(1)–Cl(1)	2.337(1)	2.339(2)	2.342(2)	2.336(1)
Pd(2)–Cl(2)			2.342(2)	2.350(1)
Pd(1)–P(1)	2.309(1)	2.335(2)	2.303(2)	2.319(1)
Pd(1)–P(2)	2.342(1)	2.313(2)	2.320(2)	2.336(1)
Pd(2)–P(3)			2.324(2)	2.314(1)
Pd(2)–P(4)			2.335(2)	2.326(1)
C(1)–P(1)	1.831(4)	1.817(5)	1.837(7)	1.837(5)
C(1)–P(4)			1.826(7)	1.840(5)
C(2)–P(2)	1.835(4)	1.837(8)	1.832(7)	1.830(5)
C(2)–P(3)			1.835(7)	1.849(5)
Pd(1)–N(1)–Pd(2)	103.7(2)	106.0(4)	109.3(3)	108.5(2)
Pd(1)–N(1)–C(3)	128.1(1)	127.0(2)	117.8(5)	134.8(3)
Pd(2)–N(1)–C(3)			131.6(5)	115.6(3)
N(1)–C(3)–C(4)	130.0(5)	139.0(7)	126.3(8)	124.8(5)
N(1)–C(3)–O(1)	115.5(4)	115.1(7)	119.5(8)	119.4(5)
O(1)–C(3)–C(4)	113.9(6)	105(1)	114.2(8)	115.8(5)
Cl(1)–Pd(1)–N(1)	176.6(1)	176.5(1)	176.7(2)	178.3(1)
Cl(2)–Pd(2)–N(1)			178.8(2)	176.5(1)
P(1)–Pd(1)–P(2)	170.1(1)	169.3(1)	173.3(1)	175.0(1)
P(3)–Pd(2)–P(4)			174.0(1)	173.6(1)
P(1)–C(1)–P(4)	114.5(2)	115.4(4)	115.2(4)	114.2(2)
P(2)–C(2)–P(3)			115.0(4)	114.4(2)

the benzoyl moieties in compounds **3b** and **3c** are disordered and this circumstance does not allow determination of some important bond distances with sufficient accuracy. The respective bond length in **3f**, however, clearly shows that the C(3)–O(1) distance is longer by *ca.* 0.08 Å than the corresponding C(7)–O(1) bond in the parent azide. The intermediate value of the C(3)–O(1) bond (1.295(7) Å) between a C(sp²)=O bond distance (1.21 Å) and a C(sp³)–O single bond length (1.41 Å) unequivocally indicates that the C=O bond has weakened compared to its strength in the free azide and has a fractional bond order between 1 and 2. It seems reasonable to suppose that a similar statement holds true for the rest of the imido complexes as well.

The availability of a good orbital overlap between the bridging N atom and the carbonyl group imposes a planar geometry around the apical nitrogen. Accordingly, the sum of the angles about the imido nitrogen approaches the ideal 360° ($\Sigma\phi(\text{N}) = 358.7\text{--}360.1^\circ$) and the displacement of the bridging nitrogen atoms from the planes determined by the Pd(1), Pd(2) and C(3) atoms does not exceed 0.1 Å. These structural peculiarities of the benzoylimido complexes recall the most outstanding structural features of carboxamides. The partial double bond character of the N–C(O) bonds of carboxamides and the hindered rotation about the N–C(O) axes have been well

documented and have been attributed to the contribution of the polar resonance form **B** to the distribution of the valence electrons along the N–C(O) fragment (Chart 1).⁴⁰

**Chart 1**

The structural peculiarities of the N–C(O) moiety in complexes **3**

Benzoyl amides have been repeatedly subjected to spectroscopic and crystallographic studies and the bonding properties of the amide moiety as well as the energetics of the rotation about the N–C(O) axis have been investigated in detail using various model compounds. In their comprehensive study, Brown and co-workers have demonstrated that the physicochemical data of various anilides and toluamides are basically consistent with the resonance model.^{40a} Where resonance is favoured, short N–C(O) bonds (1.34–1.37 Å) are formed and the rotational barriers about the N–C(O) axis are high (61–69 kJ mol⁻¹). Disfavoured resonance is, however, accompanied by the elongation of the N–C(O) bond distance (1.40–1.42 Å) and reduced barriers to rotation (25–34 kJ mol⁻¹). The $\nu(\text{CO})$ stretching band located at lower frequencies in the former and at higher frequencies in the latter case has been found to follow the structural changes. Prompted by the indisputable structural relationship of complexes **3** and the organic amides, we decided to compare some physicochemical data of these two groups of compounds.

The dynamic behaviour of the imido complexes was studied by observing their ³¹P NMR spectra at elevated temperatures. The spectral lines recorded in a DMSO-*d*₆ solution of **3a** showed broadening and merging upon stepwise increase of the temperature but coalescence was not achieved even at 448 K. Darkening of the solution indicated partial decomposition of the sample. Spectral changes of a solution of **3f** carrying the electron-donating Me₂N group could be traced up to 423 K without approaching coalescence but severe disintegration was observed at higher temperatures and the sample was rapidly destroyed at 443 K. Coalescence was observed, however, at 438 K in the case of the 2-NO₂ derivative, **3h**, which allowed us to calculate a $\Delta G^\ddagger_{\text{rot}}$ of 88.3 kJ mol⁻¹. Based on the assumption that the experimentally available highest temperature was at least lower by 10 K than that of coalescence, a $\Delta G^\ddagger_{\text{rot}} \geq 91$ kJ mol⁻¹ was derived for **3a**. Both values are much higher than the rotational barriers observed for benzoyl amides. A collection of selected physical properties associated with the dynamic behaviour of the imido complexes **3** and their organic counterparts are presented in Table 5.

Table 4 Selected bond lengths and angles of the structurally characterised benzoyl azides **2a–b** and **2f–h**

	2a	2b		2f	2g	2h	
		Molecule 1	Molecule 2			Molecule 1	Molecule 2
N(1)–N(2)	1.255(1)	1.257(2)	1.264(2)	1.247(2)	1.252(3)	1.261(3)	1.266(3)
N(2)–N(3)	1.111(1)	1.113(2)	1.110(2)	1.117(2)	1.121(3)	1.110(3)	1.103(3)
C(7)–N(1)	1.417(1)	1.410(2)	1.405(2)	1.419(2)	1.422(3)	1.411(3)	1.410(3)
C(7)–O(1)	1.202(1)	1.200(1)	1.201(1)	1.211(2)	1.218(2)	1.201(2)	1.210(2)
C(7)–C(1)	1.489(1)	1.485(2)	1.483(2)	1.467(2)	1.460(3)	1.484(3)	1.482(3)
N(1)–N(2)–N(3)	172.6(1)	175.1(1)	175.0(2)	174.1(2)	175.0(3)	173.7(2)	174.2(2)
C(7)–N(1)–N(2)	113.6(1)	111.8(1)	111.7(1)	112.8(1)	113.2(2)	112.1(2)	111.6(2)
C(1)–C(7)–N(1)	112.3(1)	112.5(1)	113.1(1)	111.8(1)	112.2(2)	112.3(2)	112.3(2)

Table 5 Selected data associated with the dynamic behaviour of *para*-substituted dimethyl benzamides and *para*-substituted benzoyl imido complexes **3**

	4-XC ₆ H ₄ C(O)NMe ₂	Imido complexes 3
$d(\text{C-N})/\text{\AA}$	1.351 ^{41a} and 1.367 ^{41b}	1.30–1.32
$\Delta G_{\text{rot}}^{\ddagger}/\text{kJ mol}^{-1}$	60.9–68.9 ^{40b}	≥ 88.3
T_{J}/K	277–317 ^{40g}	≥ 438
$\delta(^{13}\text{C})$ (ppm)	169.2–171.5 ^{40c}	171.2–174.3
$\nu(\text{CO})/\text{cm}^{-1}$	1642–1652 ^{40e}	1488–1521

Table 6 N–C(O) and C=O bond distances calculated at the B3LYP/SDDP level of DFT for [Pd₂Cl₂(μ -NC(O)Ar)(H₂PCH₂PH₂)₂] and the corresponding dimethyl benzamides

	$d(\text{C-N})/\text{\AA}$		$d(\text{C=O})/\text{\AA}$	
	3'	<i>N,N</i> -dimethyl benzamides	3'	<i>N,N</i> -dimethyl benzamides
a	1.345	1.375	1.259	1.233
e	1.349	1.380	1.259	1.234
f	1.352	1.383	1.260	1.235
h	1.335	1.367	1.254	1.231

A comparison of the N–C(O) bond lengths makes obvious that the main structural difference between the *para*-substituted benzoyl amides and complexes **3** is the remarkably short C–N distances in the latter. Besides the various pieces of crystallographic and NMR spectroscopic evidence, this is supported by the infrared absorption spectra of the complexes providing independent information on the unusual bonding properties of the imido moiety. After interactive subtraction of the IR absorption features of the dichloromethane solution of [Pd₂Cl₂(dppm)₂] and the solvent (CH₂Cl₂) from the spectra of the complexes, the appearance of two broader spectral features can be consistently observed: a strong one (showing some additional structure) around 1500 cm⁻¹ and a medium intensity band near 1350 cm⁻¹ (see Table 1), that should involve the stretching vibrations of the C(3)–O(1) carbonyl bond and the N(1)–C(3) bond, respectively. The assignments are fully supported by our DFT frequency and normal mode calculations. The fact that these frequencies (especially the former one) are outside the usual regions of carbonyl (C=O double bond, above 1600 cm⁻¹) and C–N single bond vibrations (around 1100 cm⁻¹) indicate once again that the CO bond is significantly weaker (longer) and the CN bond is stronger (shorter) than those in the corresponding amides which have no notable absorptions in the above mentioned regions.

The structural peculiarities of complexes **3** and those of dimethyl benzamides are reflected by the results of our DFT calculations (Table 6), which reveal clear differences in the structure of the N–C–O linkages in (CH₃)₂NC(O)Ar dimethyl benzamides and the corresponding [Pd₂Cl₂(μ -NC(O)Ar)(H₂PCH₂PH₂)₂] model compounds **3'** (the meaning of the letters **a**, **e**, **f**, and **h** is the same as for the unprimed series; **3**). These results indicate that the C–N bonds are systematically shorter by about 0.03 Å in palladium complexes, whereas the C–O bonds are elongated to the same extent with respect to those in the benzamide analogues.

It seems reasonable to assume that the relatively rigid nature of the N–C(O) linkage in **3** can be attributed to differences that exist in the electronic structure of the Pd–N and CH₃–N bonds. It has been postulated that the importance of the resonance form **B** depends on the ease with which a positive charge on the nitrogen is stabilised in the molecule.^{40a} As palladium is less electronegative than carbon, the Pd–N bond is more polarised than the CH₃–N linkage, which induces an excess of electron density on the imido nitrogen as compared to that in dimethyl benzamides. Indeed, the Mulliken population analysis carried out for **3e'** and the corresponding amide, C₆H₅C(O)N(CH₃)₂,

shows a notable amount of electron flow (–0.55 e) from the Pd₂Cl₂(H₂PCH₂PH₂)₂ frame towards the imido group in **3e'**, which affects mostly the N atom (the net N atomic charges in **3e'** and (CH₃)₂NC(O)(C₆H₅) are –0.51 and –0.06, respectively). The charge transfer thus enhances the ability of the N atom to donate its lone pair into the N–C(O) linkage, which strengthens the C–N bond and weakens C=O.

Although the strength of the N–C(O) bond is thought to be the primary reason of the asymmetric disposition of the benzoyl moiety, some other factors, *e.g.* the potential interaction of the carbonyl oxygen atom with the near-by palladium center, were also considered. Due to the shift of electrons from the bridging nitrogen atom toward the carbonyl group, there is a partial negative charge on the carbonyl oxygen atom and a weak C=O...Pd bonding interaction may be formed. The C=O...Pd distances in the four crystallographically characterised complexes range between 2.898 (**3f**) and 3.153 (**3b**) Å and do not differ significantly from the sum of the van der Waals radii (3.03 Å). Moreover, such interaction would probably cause the lengthening of the Pd–N and Pd–Cl bonds of the palladium center involved but this expectation is not supported by the experimental observations. Therefore, Pd...O attractions do not seem to play any role in determining the rotational barrier in complexes **3**. Consequently, the high values of the barrier to rotation in complexes **3** should be attributed to the enhanced strength of the N–C(O) bonds rather than to secondary effects.

We note, that *ortho* substituents decreasing the coplanarity of the carbonyl and aryl moieties increase the barrier to rotation in the benzoyl amide series.^{40b,d} As a reverse statement seems to be true for the ΔG^{\ddagger} values obtained for **3a** and **3h**, it seems reasonable to suppose that intramolecular interactions in **3h** not only result in a twist about the C(O)–C_{ipso} bond but also twist the C(O) group about the N–C(O) axis thereby weakening the π – π interaction within the imidocarbonyl moiety. Unfortunately, our efforts to grow single crystals of **3h** have not been successful and this conclusion could not be checked experimentally. DFT calculations carried out on the model compounds **3a'** and **3h'** did not reveal any significant differences either for the N–C(O) or the C–C_{ipso} bond lengths (see Fig. 1). The different dynamic behaviour of these complexes might be associated with intramolecular steric interactions between the dppm phenyls and the apical moieties.

Due to the scarcity of structurally characterised *N*-benzoyl-imido adducts, there is little room for a comparative discussion. In a mononuclear tungsten complex incorporating the 4-CH₃-C₆H₄C(O)N fragment as ligand,¹² the C=O bond is characteristically shorter than that in complexes **3** and the W–N linkage seems to be of a multiple-bond nature. In a tetranuclear triruthenium cobalt complex, a C=O bond length of 1.22(1) Å and a N–C(O) bond distance of 1.43(1) Å was observed⁴² within the *N*-benzoylimido μ_4 -nitrene moiety, indicating that the nitrogen lone pair is involved in N–metal coordinative bond(s). Likewise, undisturbed C=O double bonds were found in the dimolybdenum complexes [CpMoO(μ -NC(O)OEt)₂-MoOCp] and [CpMoO(μ -NC(O)OEt)(μ -O)MoOCp]^{11b} embedding *N*-ethoxycarbonyl moieties. Again, the nitrogen lone pair is shifted toward the high valent Mo(V) centers rather than toward the carbonyl group. In all these cases, the nitrogen–metal interaction is dominating in the accommodation of the nitrogen lone pair. On the contrary, donation from the nitrogen towards the neighbouring organic group has been well documented and seems to be a general behaviour of the bridging imido nitrogen in dinuclear late transition metal complexes. The $d\pi$ – π interaction of the bridging imido nitrogen atom with the sulfur atom resulted in short S–N bond distances [1.541(3)–1.565(3) Å] and a nearly planar geometry about the nitrogen atom in a series of dinuclear sulfonyl nitrene complexes of palladium.¹³ Sharp and coworkers have observed that in the aryl nitrene complex [Rh₂(CO)₂(μ -NC₆H₄NO₂-4)-

(dppm)₂] the imido nitrogen donates its electron pair towards the phenyl group and induces a quinoidal alternation of the C–C bonds in the latter.⁴³ Ongoing studies in our laboratory on the interaction of **1** with phenyl azides have revealed that the analogous [Pd₂Cl₂(μ-NC₆H₄NO₂-4)(dppm)₂] nitrene adduct possesses a trigonal planar symmetry about the bridging nitrogen atom and long (1.428(3), 1.398(4) Å) and short (1.365(3) Å) C–C bonds alternate in the 4-nitrophenyl group attached to it.⁴⁴

Structure–reactivity relationship

The structure–reactivity relationship in the reaction of aren-sulfonyl azides with [Pd₂Cl₂(dppm)₂] has been studied by kinetic⁴⁵ and structural¹⁵ investigations. It seemed of interest to us to check if a similar relationship between the structural parameters and the reactivity exists for the benzoyl azide congeners. Due to the potential thermal instability of reagents **2**, it was not our aim to conduct an extensive kinetic investigation. Instead, our studies were confined to establishing an order of reactivity at 25 °C.

Curve 1 in Fig. 4 demonstrates that the reactivity of azides **2** is significantly affected by the substituents of the phenyl moiety. The linear dependence of the relative reactivities as a function of σ constants⁴⁶ suggests that in reaction (1) the Hammett rule is obeyed. The higher reactivity of the substrates carrying electron-withdrawing substituents indicates that azides **2** act as electrophiles toward the palladium dimer. The large positive value of the ρ reaction constant (1.80) serves as evidence for the relatively larger impact of the substituents in determining the electronic properties of the azide moiety in compounds **2** compared to that with sulfonyl azides ($\rho = 1.39$ ⁴⁵).

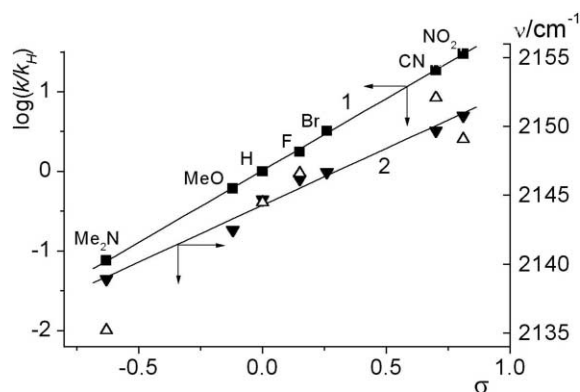


Fig. 4 Dependence of the $\log(k/k_H)$ values (solid squares) and the $\nu_{as}(N_3)$ frequencies (experimental: open triangles, DFT method, scaled data: solid triangles) on the σ constants.

A comparison of the second-order rate constant, k , of the 4-nitrobenzoyl azide ($3.9 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) with that of 4-nitrobenzenesulfonyl azide ($96.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) reveals the more moderate reactivity of the benzoyl azide reagents. Moreover, **2a**, one of the most reactive benzoyl azides, reacts even more sluggishly than the 4-methoxybenzenesulfonyl azide, the least reactive member of the sulfonyl azide series studied earlier ($k_{25} = 28.9 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$).⁴⁵ The significantly higher reactivity of the sulfonyl azide can be rationalised in terms of the more pronounced electrophilic nature of the sulfonyl group as compared to that of the carbonyl group.

In order to gain a deeper insight into the structure–reactivity relationship, we determined first the structures of the most and the least reactive benzoyl azides by means of single crystal X-ray diffraction. The common structural properties and the individual peculiarities of azides **2a**, **2b** and **2g–h** have been discussed.¹⁷ We recall here only selected data (see Table 4) that may have relevance to the structure–reactivity relationship of azides **2**.

An inspection of data presented in Table 4 demonstrates that the bond distances and angles of the azidocarbonyl moieties are only moderately affected by the electronic nature of the substituents. The most characteristic structural data supporting the expectation that substituents do influence the bondings at the reactive end of the molecules are the differences between the N(1)–N(2) and N(2)–N(3) bonds. The deviation of the two N–N bond lengths (Δd_N) is relatively large for the electron-withdrawing nitro- (**2h**: 0.157 Å, **2a**: 0.147 Å) and cyano-groups (**2b**: 0.149 Å) and noticeably shorter for **2f** (0.130 Å) and **2g** (0.131 Å), both carrying electron-releasing substituents. The larger value of Δd_N for **2a**, **2b**, and **2h** is in favour of an increased contribution of the canonical form **D** (Chart 2) to the resonance hybrid when electron-withdrawing substituents are present and also suggests the azide to be more electrophilic. We note that an analogous trend of the Δd_N differences has been observed for sulfonyl azides.^{15,17}

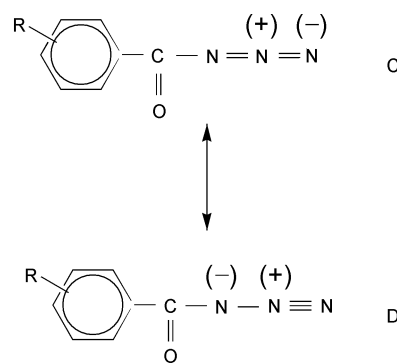


Chart 2

Although the C(7)–O(1) and C(7)–C(1) distances show changes that can be explained in terms of inductive and mesomeric effects of R groups, other data presented in Table 4 demonstrate the insensitivity of the structural parameters to the electronic properties of the substituent.

IR spectroscopy has been an efficient tool for the structural characterisation of organic azides. In the case of benzoyl derivatives, however, observation of the N₃ stretching bands does not offer an instant help in understanding how the substituents influence the bonding properties of the azido group because the $\nu_{as}(N_3)$ bands (the corresponding normal mode has a prevailing contribution from the stretching vibration of the terminal N≡N bond) observed in the 2200–2100 cm⁻¹ region show splitting of varying extent. The phenomenon has been explained in terms of Fermi resonance with the combination mode of the $\nu_s(N_3)$ vibration around 1180 cm⁻¹ and the aromatic ring vibration at 990 cm⁻¹ falling in the same region.⁴⁷ Based on the well known principles of Fermi resonance⁴⁸ (taking into account the anharmonicity of the vibrations involved as well), we have made some efforts to calculate the unperturbed frequency of the $\nu_{as}(N_3)$ vibration, *i.e.* locate the position ν° of this band in the IR spectra of all azides studied. Our efforts to find the $\nu_{as}^\circ(N_3)$ frequencies were successful with six benzoyl azides but, unfortunately, gave doubtful results with **3c** and **3f** where the picture was complicated by the presence of more than two potentially interacting bands. The positions of the pairs of observed components of the $\nu_{as}(N_3)$ doublet, the corrected $\nu_{as}^\circ(N_3)$ values obtained with reasonable certainty as well as the frequencies of the $\nu(C=O)$ stretching bands are collected in Table 7. Two more columns contain, for comparison, frequencies of $\nu_{as}^\circ(N_3)$ and $\nu(C=O)$ vibrations calculated at the B3LYP/SDDP level of DFT. They are available for all nine molecules, and are unaffected by uncertainties connected to Fermi resonance or experimental difficulties.

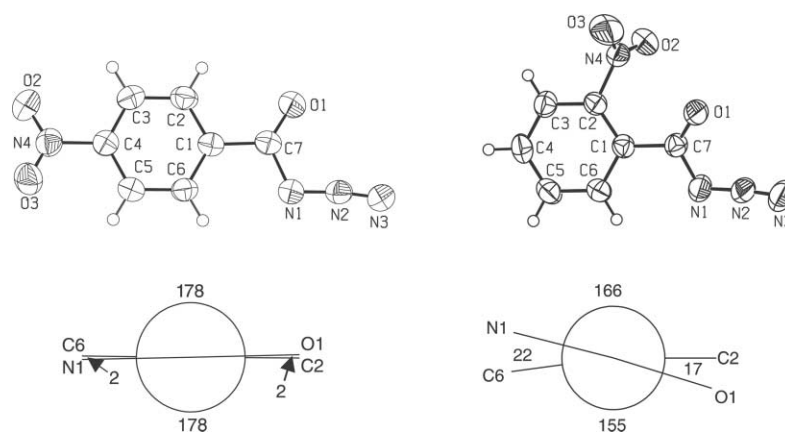


Fig. 5 Molecular structures and Newman projections of benzoyl azides **2a** (left) and **2h** (right).

Table 7 The experimental and the calculated positions of the $\nu_{\text{as}}(\text{N}_3)$ and $\nu(\text{C}=\text{O})$ bands and the relative reactivities of benzoyl azides **2**

	Observed in IR spectra			DFT calculated data		
	$\nu_{\text{as}}(\text{N}_3)$	$\nu_{\text{as}}^\circ(\text{N}_3)$	$\nu(\text{C}=\text{O})$	$\nu_{\text{as}}^\circ(\text{N}_3)^a$	$\nu(\text{C}=\text{O})^b$	k/k_{H}
2a	2178.6	2149.1	1701.2	2150.8 (2259.2)	1702.1 (1765.7)	30.0
2b	2180.7	2152.1	1701.1	2149.7 (2258.1)	1700.8 (1764.3)	18.6
2c	2178.1		1696.0	2146.7 (2254.9)	1699.4 (1762.9)	3.2
2d	2178.3	2146.6	1698.5	2146.2 (2254.4)	1698.7 (1762.1)	1.8
2e	2173.8	2144.5	1699.5	2144.7 (2252.8)	1699.6 (1763.1)	1
2f	2174.6		1693.5	2142.5 (2250.5)	1693.9 (1757.2)	0.61
2g	2173.0	2135.2	1684.1	2138.9 (2246.7)	1687.8 (1750.8)	0.08
2h	2171.9	2151.7	1713.1	2149.0 (2257.4)	1709.8 (1773.7)	
2i	2216.8		1706.0	2153.5 (2262.1)	1705.1 (1768.8)	

^a The raw calculated values (in parentheses) scaled by 0.952. ^b The raw calculated values (in parentheses) scaled by 0.964. ^c The major component of the $\nu_{\text{as}}(\text{N}_3)$ band involved in Fermi resonance.

From the data presented in Table 7 we can conclude that the positions of the doublets ascribed to the N_3 asymmetric stretching band vary only negligibly with the electronic nature of the substituent. The corrected $\nu_{\text{as}}^\circ(\text{N}_3)$ frequencies do show, however, the expected dependence, *viz.* a shift of N_3 stretching band toward higher wave numbers on going from electron-releasing to electron-withdrawing substituents.

The trend of the ν° values is in line with the observed difference of the N–N bonds discussed above and also coincides with the shift of the $\nu_{\text{as}}(\text{N}_3)$ frequencies reported earlier for sulfonyl azides.¹⁵ While the position of the $\nu_{\text{as}}(\text{N}_3)$ band has proved to be a most convenient parameter to estimate the relative reactivities of sulfonyl azides, in the case of the benzoyl congeners, however, it is the position of the $\nu_{\text{as}}^\circ(\text{N}_3)$ band (obtained from the observed IR spectra or from DFT calculation) that most closely reflects the reactivity of the azide reagents (Fig. 4, curve 2).

Finally, we would like to draw attention to the differences emerging between the structural parameters and the reactivity of benzoyl azides carrying a nitro substituent in *para* (**2a**) or *ortho* (**2h**) positions. As shown by kinetic investigations, 2-nitrobenzoyl azide is the most reactive member of azides **2a–2h**. The more pronounced tendency of **2h** to form imido complexes was demonstrated by the rate constants ($k_{2\text{h}} = 23 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$; $k_{2\text{a}} = 3.9 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) and also by the product distribution when the reaction was conducted under pseudo-first-order conditions ($[\mathbf{3h}]/[\mathbf{3a}] = 6$, see Experimental section).

Table 8 Selected structural data of benzoyl azides **2a** and **2h**

2a		2h
0.147	$\Delta d_{\text{N}}/\text{\AA}$	0.157
–1.8(2)	$\phi[\text{C}(2)–\text{C}(1)–\text{C}(7)–\text{O}(1)]^\circ$	18.8(2), mean
2149.1	$\nu_{\text{as}}^\circ(\text{N}_3)/\text{cm}^{-1}$ (experimental)	2151.7
1701.2	$\nu(\text{CO})/\text{cm}^{-1}$ (experimental)	1713.1

Fig. 5 presents the molecular structures and the Newman projections of **2a** and **2h**. Selected IR and crystallographic data of the same compounds are given in Table 8. The drawings clearly show that the steric interaction between the carbonyl and nitro groups in **2h** not only twists the latter about the C(2)–N(4) bond but hampers the ideal coplanar arrangement of the phenyl ring with the carbonyl moiety (see the respective dihedral angles in Table 8). The weakened conjugation of the carbonyl group towards the phenyl ring makes the CO unit more electrophilic, which, in turn, results in a more efficient polarisation of the azido group. Both the IR spectroscopic data and the differences of the N–N bonds reflect the different geometry of the two azides and predict **2h** to be the most reactive member of the series examined. We note that the increased barrier to rotation observed with various *ortho*-substituted benzamides has also been attributed to a decreased conjugation of the carbonyl and phenyl groups.^{40b}

We feel it important to mention at this point that structural data predicted the enhanced reactivity of 2-nitrobenzenesulfonyl azide over the 4-nitro derivative but this expectation was not proved experimentally.¹⁵ The question why a potentially higher reactivity can prevail with benzoyl azides but cannot be effective with the benzenesulfonyl azide congeners remains unanswered at the moment. We think that a detailed analysis of the reaction mechanism with special attention to intramolecular steric interactions could be of help in this matter.

Conclusions

The reaction of benzoyl azides with $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$ has proved to be an efficient route for the preparation of dinuclear *N*-benzoylnitrene complexes of palladium. The novel complexes possess surprisingly strong N–C(O) bonding as demonstrated by the high values of $\Delta G^\ddagger_{\text{rot}} (\geq 88.3 \text{ kJ mol}^{-1})$ and $T_c (\geq 438 \text{ K})$. The unusually strong double bond character of the N–C(O) linkage in complexes **3** is attributed to $\pi\text{–}\pi$ interaction of the nitrogen and carbon atoms supported by the electron rich palladium centers. It is believed that the Pd–N bonds enhance the electron shift towards the carbonyl group by stabilising the positive charge on the bridging nitrogen atom. The steric interaction of the nitro and carbonyl groups in 2-nitrobenzoyl azide is seen as the primary reason of the outstanding structural features and the enhanced reactivity of this reagent.

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