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PAPER

Anhydrous TEMPO-H: reactions of a good hydrogen atom donor with low-valent carbon centres†

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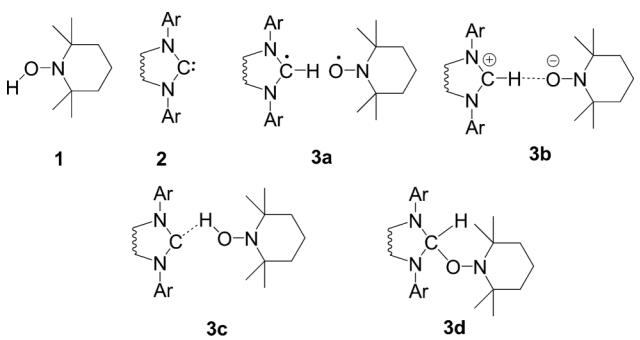
In this paper, we report a novel synthesis of anhydrous 1-hydroxy-2,2,6,6-tetramethyl-piperidine (TEMPO-H). An X-ray crystal structure and full characterization of the compound are included. Compared to hydrated TEMPO-H, its anhydrous form exhibits improved stability and a differing chemical reactivity. The reactions of anhydrous TEMPO-H with a variety of low-valent carbon centres are described. For example, anhydrous TEMPO-H was reacted with 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes), an unsaturated NHC. Crystals of $[CHNC_6H_2(CH_3)_3]_2C\cdots HO(NC_5H_6(CH_3)_4)$, IMes $\cdots$ TEMPO-H, were isolated and a crystal structure determined. The experimental structure is compared to the results of theoretical calculations on the hydrogen-bonded dimer. Anhydrous TEMPO-H was also reacted with the saturated NHC, 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene (SIPr), giving the product $[CH_2N\textit{i}\text{-}Pr_2C_6H_3]_2CH\cdots O(NC_5H_6(CH_3)_4)$. In contrast, the reaction of hydrated TEMPO-H with 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene gave small amounts of the hydrolysis product, *N*-(2,6-diisopropylphenyl)-*N*-[2-(2,6-diisopropylphenylamino)ethyl]formamide. Finally, anhydrous TEMPO-H was reacted with (triphenylphosphoranylidene)ketene to generate $Ph_3PC(H)C(=O)O(NC_5H_6(CH_3)_4)$. A full characterization of the product, including an X-ray crystal structure, is described.

Introduction

We have had a long standing interest in the reactivity of low-valent main group compounds with protons, hydride and the hydrogen atom.[1] We have successfully detected unusual hydrogen bonds in a variety of instances, and have also observed transient radicals using EPR and/or muon spectroscopy.[2] Recently, we detected a radical derived from the addition of muonium, a hydrogen atom surrogate, to an *N*-heterocyclic carbene (NHC),[3,4] and also identified a related radical *via* the electrochemical reduction of an imidazolium ion. The intermediate radical was observed using EPR spectroscopy.[5] Here, we report some chemical reactions of one of the best chemical sources of hydrogen atoms (1-hydroxy-2,2,6,6-tetramethylpiperidine, TEMPO-H; **1**) with several molecules possessing low-valent carbon centres, including two NHCs and (triphenylphosphoranylidene)ketene.[6] The reactions reported herein are relevant to a number of NHC-catalyzed oxidation reactions, where NHCs and TEMPO/TEMPO-H are important in catalytic cycles.[7,8]

The combination of **1** with NHCs (**2**) can theoretically give rise to a number of radical, neutral or ionic alternatives (Scheme 1). Specifically, **3a** represents the radical reaction product derived from hydrogen atom transfer, **3b** is the charge-separated species, **3c** is the hydrogen-bonded derivative and **3d** can be considered the O–H insertion product.



Scheme 1 Structural isomers formed by the reaction of TEMPO-H (**1**) with NHCs (**2**).

Access to anhydrous TEMPO-H has not been reported in the literature, but it was clear to us early on that the water in

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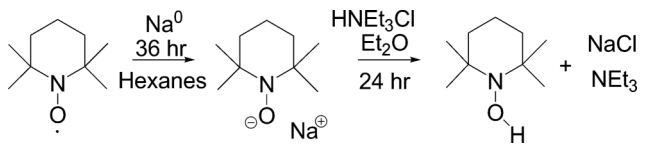
TEMPO-H could result in unwanted side reactions (*vide infra*). Here, we report the preparation of anhydrous TEMPO-H, show that its reactivity does indeed differ from that of hydrated TEMPO-H and report its chemistry with some low-valent carbon centres.

Results and discussion

We have been interested in the reaction of protic reagents with a variety of main group compounds for some time. In general, we have always observed the formation of diamagnetic materials, so we decided to explore the addition of a protic reagent, where addition of the proton could occur, but where there was also some possibility of hydrogen atom addition resulting in radical formation. We had considerable experience working with a variety of reactive main group compounds and began this investigation from the literature preparation of TEMPO-H, a sensitive solid isolated as a hydrate.

Noting the high reactivity of low-valent carbon compounds with water, we prepared anhydrous **1** using a new route, as shown in Scheme 2. The sodium salt of TEMPO was prepared and isolated according to the literature.[9] It was subsequently treated with triethylamine hydrochloride, producing **1** in approximately 54% yield.



Scheme 2 Preparation of anhydrous TEMPO-H.

The full characterization matched the spectroscopic data found in the literature, with the exception of those data consistent with the presence of water in the material. The crystal structure of anhydrous TEMPO-H was determined and is shown in Fig. 1. Selected bond lengths and angles for the structures presented in this work are listed in Table 1.

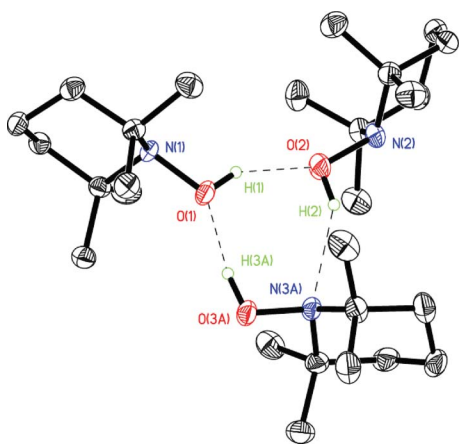


Fig. 1 Crystal structure (50% probability ellipsoids) of the anhydrous TEMPO-H (**1**) trimer, showing the [N···H–O] and [O···H–O] hydrogen bonds.

Anhydrous TEMPO-H crystallizes in the trigonal space group $R\bar{3}$, with three unique molecules in the asymmetric unit. The three discrete molecules are held together as a single, closed cyclic unit by the three hydrogen bonds (Table 2). There are two O–H···O type hydrogen bonds and one relatively weaker O–H···N type bond holding the trimer together.

The crystal structure of the related, hydrated TEMPO-H was reported by Mader *et al.* in 2007.[10] This structure also has three molecules (and one molecule of water) in the asymmetric unit and is held together in a hydrogen-bonded network (shown in Fig. 2), but it crystallizes in the lower symmetry, triclinic space group $P\bar{1}$. The hydrogen bonds in the crystal structure of hydrated TEMPO-H (listed in Table 2) involve not only the donor H(O) protons of the TEMPO-H itself but also those of the solvated water molecules. Although the authors describe the hydrogen bonds as forming a chain, the hydrogen bonded unit formed is actually a closed structure involving a total of six TEMPO-H molecules (two of each unique type) and two water molecules. The hydrogen bonding of hydrated TEMPO-H is shown in Fig. 2; the diagram was generated using data deposited in the Cambridge Structural Database.[11] The two very different hydrogen bonding motifs in TEMPO-H and hydrated TEMPO-H must arise from the involvement of the water molecule in the hydrogen bonding pattern of the latter and result in the two compounds crystallizing in very different crystal systems and space groups.

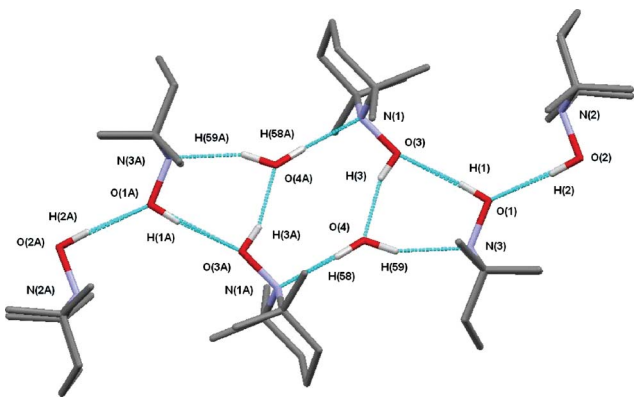


Fig. 2 TEMPOH·$\frac{1}{3}$H$_2$O crystal structure showing the [N···H–O] and [O···H–O] hydrogen bonding arrangement. The diagram was generated using data deposited in the Cambridge Structural Database[11] and the Mercury program for visualization.[12]

The N–O bond length in anhydrous TEMPO-H (this work) averages 1.459(2) Å, similar to the average value reported in hydrated TEMPO-H (1.456(6) Å) by Mader *et al.*[10] These authors noted that this is substantially longer than the N–O distance observed in TEMPO[13] (1.284(8) Å) because the N–O bond in the radical has partial π character.

Finally, from a synthetic point of view, anhydrous TEMPO-H is much more stable than hydrated TEMPO-H, and does not as readily decompose to TEMPO during work-up and purification by sublimation. Anhydrous TEMPO-H is prepared under an inert atmosphere, where it can be kept indefinitely in the absence of water; storing it at low temperature (–35 °C) impedes its loss by sublimation. In addition, anhydrous TEMPO-H is highly reactive. In all of the reactions performed for this study, all the products were diamagnetic species, as indicated by their sharp ^{1}H and ^{13}C NMR resonances. The spectroscopic data indicates that structures of the type **3a** were not formed.

Table 1 Selected structural data (bond lengths [Å] and angles [°]) for the reported compounds

Anhydrous TEMPO-H		IMes···TEMPO-H		$[CH_2N\textit{i}\text{-}Pr_2C_6H_3]_2CH\cdots OC_6H_2CH_3(C(CH_3)_3)_2]$		$Ph_3PC(H)C(=O)ON(C_5H_6(CH_3)_4)$	
(for one of the three molecules in the unit cell)							
C(1)–N(1)	1.4884(19)	N(1)–C(1)	1.3629(17)	N(1)–C(1)	1.309(3)	P(1)–C(1)	1.8065(15)
C(1)–C(7)	1.534(2)	N(1)–C(2)	1.3905(18)	N(1)–C(2)	1.478(3)	P(1)–C(7)	1.8085(14)
C(1)–C(2)	1.536(2)	N(1)–C(4)	1.4446(16)	N(1)–C(4A)	1.478(9)	P(1)–C(13)	1.8086(15)
C(1)–C(6)	1.542(2)	N(2)–C(1)	1.3648(16)	N(1)–C(4B)	1.399(9)	P(1)–C(19)	1.7075(14)
C(2)–C(3)	1.520(2)	N(2)–C(3)	1.3913(18)	N(2)–C(1)	1.321(3)	C(19)–H(19)	0.966(18)
C(3)–C(4)	1.520(2)	N(2)–C(13)	1.4422(17)	N(2)–C(3)	1.477(3)	C(19)–C(20)	1.4046(19)
C(4)–C(5)	1.535(2)	N(3)–O(1)	1.4448(14)	N(2)–C(16)	1.466(3)	O(1)–C(20)	1.3944(16)
C(5)–N(1)	1.4932(19)	N(3)–C(26)	1.4895(17)	C(1)–H(1)	1.00(3)	O(2)–C(20)	1.2315(17)
C(5)–C(9)	1.529(2)	N(3)–C(22)	1.4898(17)	C(2)–C(3)	1.303(3)	N(1)–O(1)	1.4562(15)
C(5)–C(8)	1.541(2)	O(1)–H(1)	0.96(2)	O(1)–C(28)	1.519(4)	N(1)–C(21)	1.4950(19)
N(1)–O(1)	1.4503(16)	C(2)–C(3)	1.340(2)	C(28)–C(29)	1.437(4)	N(1)–C(25)	1.4955(19)
O(1)–H(1)	0.89(2)	C(22)–C(23)	1.532(2)	C(28)–C(33)	1.435(4)	C(21)–C(22)	1.531(2)
		C(23)–C(24)	1.523(2)	C(29)–C(30)	1.384(4)	C(22)–C(23)	1.519(2)
		C(24)–C(25)	1.523(2)	C(30)–C(31)	1.394(4)	C(23)–C(24)	1.521(2)
		C(25)–C(26)	1.524(2)	C(31)–C(32)	1.377(4)	C(24)–C(25)	1.541(2)
				C(32)–C(33)	1.395(4)		
N(1)–C(1)–C(7)	106.14(12)	C(1)–N(1)–C(2)	112.64(11)	C(1)–N(1)–C(2)	111.1(2)	C(1)–P(1)–C(7)	106.02(6)
N(1)–C(1)–C(2)	106.37(12)	C(1)–N(1)–C(4)	122.89(11)	C(1)–N(1)–C(4A)	129.2(12)	C(1)–P(1)–C(13)	105.79(7)
C(7)–C(1)–C(2)	109.04(13)	C(2)–N(1)–C(4)	124.27(11)	C(1)–N(1)–C(4B)	126.9(12)	C(7)–P(1)–C(13)	105.83(7)
N(1)–C(1)–C(6)	115.89(13)	C(1)–N(2)–C(3)	112.43(11)	C(2)–N(1)–C(4A)	119.6(12)	C(19)–P(1)–C(1)	117.21(7)
C(7)–C(1)–C(6)	108.06(13)	C(1)–N(2)–C(13)	123.10(11)	C(2)–N(1)–C(4B)	122.0(12)	C(19)–P(1)–C(7)	108.03(7)
C(2)–C(1)–C(6)	111.08(13)	C(3)–N(2)–C(13)	124.31(11)	C(1)–N(2)–C(3)	109.9(2)	C(19)–P(1)–C(13)	113.19(7)
C(3)–C(2)–C(1)	112.98(13)	O(1)–N(3)–C(26)	107.30(10)	C(1)–N(2)–C(16)	126.2(2)	P(1)–C(19)–H(19)	119.5(10)
C(2)–C(3)–C(4)	109.08(13)	O(1)–N(3)–C(22)	107.30(10)	C(3)–N(2)–C(16)	120.7(2)	C(20)–C(19)–P(1)	116.19(11)
C(3)–C(4)–C(5)	113.53(13)	C(26)–N(3)–C(22)	118.62(10)	N(1)–C(1)–N(2)	112.1(2)	C(20)–C(19)–H(19)	123.8(11)
N(1)–C(5)–C(9)	106.39(12)	N(3)–O(1)–H(1)	103.3(12)	N(1)–C(1)–H(1)	121.3(15)	O(1)–C(20)–C(19)	120.89(13)
N(1)–C(5)–C(4)	106.12(12)	N(1)–C(1)–N(2)	102.23(11)	N(2)–C(1)–H(1)	126.6(15)	O(2)–C(20)–C(19)	126.32(13)
C(9)–C(5)–C(4)	108.83(13)	C(3)–C(2)–N(1)	106.27(12)	N(1)–C(2)–C(3)	101.9(2)	O(2)–C(20)–O(1)	112.77(11)
N(1)–C(5)–C(8)	116.02(13)	C(2)–C(3)–N(2)	106.43(12)	N(2)–C(3)–C(2)	103.0(2)	C(20)–O(1)–N(1)	115.58(9)
C(9)–C(5)–C(8)	108.30(13)	N(3)–C(22)–C(23)	107.26(11)	O(1)–C(28)–C(29)	121.6(2)	O(1)–N(1)–C(21)	106.17(10)
C(4)–C(5)–C(8)	110.92(13)	C(24)–C(23)–C(22)	112.89(13)	O(1)–C(28)–C(33)	121.4(3)	O(1)–N(1)–C(25)	106.65(10)
O(1)–N(1)–C(1)	107.44(11)	C(23)–C(24)–C(25)	109.04(12)	C(29)–C(28)–C(33)	116.9(2)	C(21)–N(1)–C(25)	119.32(11)
O(1)–N(1)–C(5)	106.68(11)	C(24)–C(25)–C(26)	113.17(12)	C(28)–C(29)–C(30)	119.8(2)	N(1)–C(21)–C(22)	106.53(12)
C(1)–N(1)–C(5)	119.71(12)	N(3)–C(26)–C(25)	107.39(11)	C(29)–C(30)–C(31)	123.2(3)	C(23)–C(22)–C(21)	112.78(13)
N(1)–O(1)–H(1)	105.8(12)			C(30)–C(31)–C(32)	116.8(3)	C(22)–C(23)–C(24)	109.16(13)
				C(31)–C(32)–C(33)	123.7(3)	C(23)–C(24)–C(25)	113.24(13)
				C(28)–C(33)–C(32)	119.3(3)	N(1)–C(25)–C(24)	106.41(12)

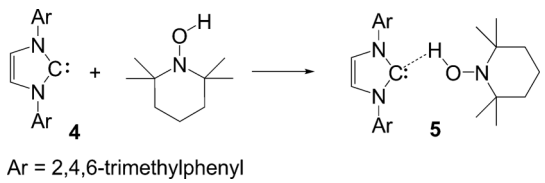
Table 2 Hydrogen bond distances and angles in anhydrous and hydrated TEMPO-H

	D–H···A	d(D–H)/Å	$d_{H\cdots A}$/Å	$d_{D\cdots A}$/Å	(DHA) (°)	Symmetry of acceptor
TEMPOH	O1–H1···O2	0.89(2)	1.89(2)	2.7172(16)	152.1(17)	x, y, z
	O2–H2···N3	0.89(2)	2.50(2)	3.2953(17)	149.0(18)	$x, y+1, z$
	O3–H3···O1	0.94(2)	1.83(2)	2.7562(16)	169.2(19)	$x, y-1, z$
TEMPOH·$\frac{1}{3}H_2O$	O2–H2···O1	0.89(2)	1.94(2)	2.830(2)	175(2)	x, y, z
CCDC Refcode[11]	O1–H1···O3	0.88(2)	2.00(2)	2.882(2)	173(2)	x, y, z
UDENOH	O3–H3···O4	0.83(3)	1.86(2)	2.685(2)	158(3)	x, y, z
	O4–H58···N1	0.99(3)	1.922	2.885	164.2	$-x, 1-y, 1-z$
	O4–H59···N3	0.94(3)	2.079	2.970	158.2	x, y, z

The differing reactivity of hydrated TEMPO-H *vs.* its anhydrous form is clearly illustrated by their respective reactions with the saturated NHC, 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene (SiPr) (Scheme 3). In our hands, the reaction with hydrated TEMPO-H gave *N*-(2,6-diisopropylphenyl)-*N*-[2-(2,6-diisopropylphenylamino)ethyl]formamide as the hydrolysis product. The product was identified by comparison with literature data previously reported for the same compound by Günay *et al*.[14] In their work, Günay *et al.* obtained the identical compound from the reaction of 1,3-bis(4-dimethylaminobenzyl)imidazolinium chloride with *N*,*C*-type palladacyclic acetate in a 2 : 1 ratio in THF (not their anticipated product). They speculated that the free NHC or the corresponding carbene dimer must have been generated initially, followed by insertion into a water H–OH bond to give the observed hydrolysis product. They report that previous studies on the reactivity of NHCs showed that the saturated ring reacts

instantly with water to give formamide derivatives, and that the hydrolysis necessitates the study of NHC complex formation in anhydrous media. In our case, the water present in hydrated TEMPO-H must be the source of the water necessary for hydrolysis to occur. In contrast, the reaction with anhydrous TEMPO-H gives a single product (*vide infra*). We anticipate that the reaction of hydrated TEMPO-H with IMes should also result in the hydrolysis of the NHC rather than a reaction with the TEMPO-H substrate, based on the results recently reported by Hollóczki *et al*.[15] The increased stability during preparation, the improved chances of isolating tractable products from reaction, and the possibility of differing chemistry make anhydrous TEMPO-H a reagent worthy of further investigation.

The reaction of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), an unsaturated NHC, with anhydrous TEMPO-H in hexanes resulted in the formation of a clear solution (Scheme 3). Filtration and crystallisation by slow evaporation of solvent resulted in the isolation of clear, light yellow crystals.



Scheme 3 Reaction of TEMPO-H with an *unsaturated* NHC.

NMR solution studies of the crystalline product in C_6D_6 revealed signals for a 1 : 1 complex of TEMPO-H and IMes. Diagnostic peaks were observed at 210.9 ppm in the $^{13}C\{^1H\}$ NMR spectrum, consistent with the presence of the NHC carbeneic carbon centre, and a TEMPO-H O*H* resonance occurs at 8.38 ppm, very close to the resonance observed for free TEMPO-H (8.36 ppm) in the same solvent. The analytical data, as well as the elemental analysis, were in accord with a 1 : 1 complex of **1** with the NHC. We note that in C_6D_6 a reaction slowly occurs and we are unsure of the product.

In an attempt to resolve the connectivity of the components, a single crystal X-ray structural determination was performed, the results of which are shown in Fig. 3. The most distinctive feature of the crystal structure is the O–H···C hydrogen bond that links the TEMPO-H molecule to the IMes ring. Hydrogen atom H1 was refined isotropically and found to still be covalently bonded to O1 of TEMPO with a slightly elongated O1–H1 bond length of 0.96(2) Å. The hydrogen bond is characterized by a H1···C1 distance of 1.91(2) Å, an O1···C1 distance of 2.854(2) Å and an O1–H1···C1 angle of 170(2)°.

There are only two related structures, with similar O–H···C (IMes) hydrogen bonds reported in the literature, an IMes···methanol complex reported by Movassaghi and Schmidt[16] in 2005, and an IMes···triphenylmethanol complex reported by the same group in 2008.[17] The length of the hydrogen bond O···C interaction in the current complex, 2.854(2) Å, is very close to that found in the triphenylmethanol adduct, 2.856(3) Å, and slightly longer than that in the methanol complex, 2.832(2) Å. In the TEMPO-H···IMes complex, the oxygen (O1) and hydrogen (H1) atoms sit 0.597(3) and 0.28(2) Å, respectively, from the plane defined by the five atoms of the imidazolylidene ring, allowing the formation of quite a linear hydrogen bond, 170(2)°. Again,

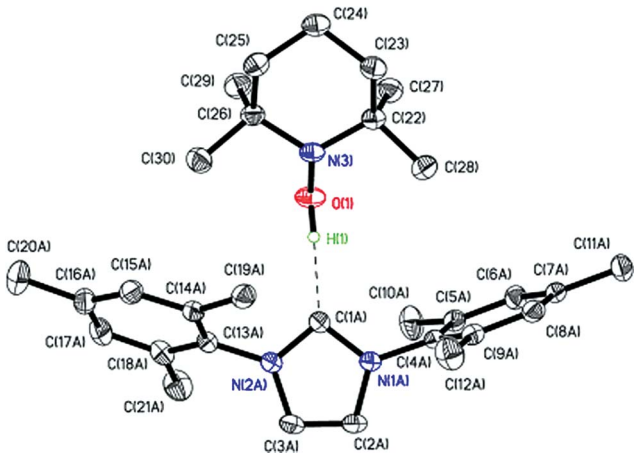


Fig. 3 Crystal structure (50% probability ellipsoids) of the IMes···TEMPO-H adduct $[CHNC_6H_2(CH_3)_3]_2C\cdots HO(NC_5H_6(CH_3)_4)$, showing the [C···H–O] hydrogen bond. The symmetry used to generate the IMes molecule is $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

this is midway between the angles reported for the methanol and triphenylmethanol complexes, 174 and 166°, respectively.

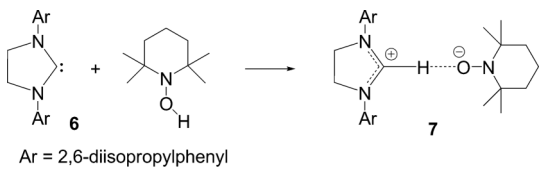
Movassaghi and Schmidt[16] discuss the N–C–N angle within the imidazolium ring as being indicative of the degree of proton transfer (*i.e.* the strength of the hydrogen bond). Hydrogen bond formation is expected to relax the N–C–N bond angle of the carbene toward that found in an imidazolium ion. The N–C–N bond angle of the TEMPO-H···IMes complex is 102.23(11)°, which is closer to the observed angle in the free carbene (101.4°)[18] than that in imidazolium chloride (108.6°).[19] The angle observed here is midway between that found in the methanol complex (102.53(16)°) and that found in the triphenylmethanol complex (101.9(2)°).

Ab initio calculations were carried out to investigate the intermolecular hydrogen bonding and electronic structure of the complex formed when *N*,*N*′-dimethylimidazol-2-ylidene ("NHC") reacts with the TEMPO radical (see the Experimental section for calculation details). *N*,*N*′-Dimethylimidazol-2-ylidene exists as a C_{2v} symmetric structure while the free TEMPO radical exists in a C_s symmetric chair conformation. The calculated value for the reaction TEMPO + $\frac{1}{2}$ H_2 → TEMPO-H is exothermic (52 kJ mol^{-1}). TEMPO-H exists in one of two possible chair conformations, with the abstracted hydrogen in either a synclinal or an anticlinal arrangement with respect to both N–C bonds. The anticlinal arrangement is 15 kJ mol^{-1} more stable than the synclinal arrangement; the boat conformation is not stable with respect to the other conformations.

"NHC" interacts with TEMPO-H to form a complex that is 33 kJ mol^{-1} more stable than the reactants, TEMPO-H and free "NHC". The N–C–N angle in free "NHC" relaxes a small amount and goes to 103.0° upon complexation. The O–H bond distance increases from 0.970 Å in TEMPO-H to 1.001 Å in the complex. The vibrational frequencies (B3LYP/6-31+G*, unscaled) of the modes predominantly involving the hydrogen (O–H) undergo significant changes upon complexation. The stretching frequency drops from 3746 to 3146 cm^{-1}. The NOH bending mode increases from 1341 to 1556 cm^{-1} and the torsion about the N–O bond increases from 373 to 903 cm^{-1}. These trends are all consistent with a hydrogen bonding interaction between the carbene lone

pair and the acidic hydrogen of TEMPO-H, as also observed in the X-ray crystal structure.

The reaction of anhydrous TEMPO-H with the saturated NHC 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene[20] in hexanes resulted in the formation of a single product, as indicated by the spectroscopic data (Scheme 4). The ^{1}H NMR exhibited a singlet at 9.17 ppm, integrating for one hydrogen, and the OH resonance for TEMPO-H was no longer observed. In the ^{13}C NMR spectrum, the resonance for the carbeneic NHC carbon was no longer evident but a signal (163 ppm) corresponding to a new CH fragment, diagnostic of an imidazolidinium cation, was present. Although no crystalline product was ever isolated, even after multiple attempts, we believe the product to be the saturated SIPr$\cdots$TEMPO-H adduct $[CH_2N\textit{i}\text{-}Pr_2C_6H_3]_2CH\cdots O(NC_5H_6(CH_3)_4)$.



Scheme 4 Reaction of TEMPO-H with a *saturated* NHC.

To help confirm the nature of the product formed in the above reaction, we deliberately protonated the saturated NHC 1,3-bis(2,6-diisopropyl-phenyl)imidazolidin-2-ylidene with 2,6-di-*t*-butyl-phenyl-4-methylphenol (BHT)[20] and confirmed its structure by X-ray crystallography. The successful solution and refinement of the structure showed that an ionic product had been formed between the two constituents, without solvation and with only one unique cation and anion in the asymmetric unit. The orthorhombic space group $P2_12_12_1$ (#19) proved most suitable for refinement. Although the data was collected at 100 K, the structure was found to be highly disordered. It contains a strong C–H$\cdots$O hydrogen bond that holds the cation and anion together, as shown in Fig. 4. The C1–H1$\cdots$O1 (O1 symmetry $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$) hydrogen bond is characterized by a C–H bond length of 1.00(3) Å, an H$\cdots$O distance of 1.89(3) Å, a C$\cdots$O distance of 2.886(3) Å and an almost linear C–H$\cdots$O angle of 175(2)°.

The cation maintains a saturated C2–C3 bond with a bond length of 1.519(4) Å and two hydrogen atoms clearly visible on each carbon centre in the Fourier difference map. This is in keeping with the structural details reported by Giffin *et al.*[21] for 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene. The unprotonated starting material crystallizes in the monoclinic space group $P2_1/c$ and this structure is also somewhat disordered. In the neutral saturated compound, the C2–C3 bond length is a comparable 1.514(3) Å. Protonation at C1 has definite consequences for the structural parameters of the ring. In the neutral complex, the C1–N bond lengths are 1.346(2) Å (to N1) and 1.347(2) Å (to N2), and the N1–C1–N2 angle is 104.98(11)°. Protonation results in a shortening of the C1–N bonds, 1.309(3) Å to N1 and 1.321(3) Å to N2, with a concurrent increase in the N1–C1–N2 angle to 112.1(2)°. The ring in the protonated cation remains quite planar; using the five ring atoms to define a plane, the mean deviation from this plane is only 0.060 Å, with C3 lying farthest out of the plane at –0.080(2) Å.

A structure closely related to the current one was reported by Cowan *et al.* in 2002.[22] The unsaturated NHC 1,3-

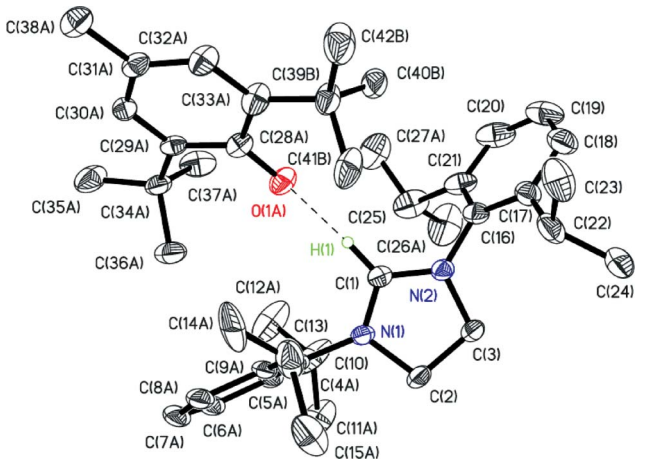


Fig. 4 Crystal structure (50% probability ellipsoids) of the saturated NHC$\cdots$phenol adduct $[CH_2N\textit{i}\text{-}Pr_2C_6H_3]_2CH\cdots OC_6H_2CH_3(C(CH_3)_3)_2$, showing the [O$\cdots$H–C] hydrogen bond. Hydrogen atoms (except for H1) and the minor component of all the disordered portions of the molecule have been removed for clarity. The symmetry used to generate the BHT molecule is $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

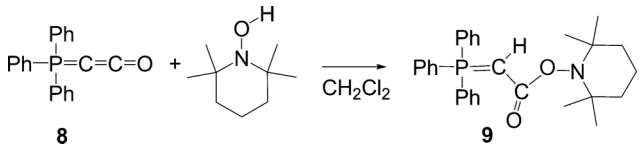
dimesitylimidazol-2-ylidene was also found to react with 2,6-di-*t*-butyl-4-methylphenol to give a protonated salt with unusually short C–H$\cdots$O hydrogen bonds. In the structure, ion pairs are associated through strong C–H$\cdots$O interactions: C1–H1$\cdots$O1: D = 2.801(4) Å, d = 1.87(3) Å, θ = 175(2)°; C4–H4$\cdots$O2: D = 2.842(4) Å, d = 1.88(3) Å, θ = 169(2)°. The authors report that these interactions are significantly shorter than any previously reported hydrogen bonds between CH donors and O acceptors. The C–H$\cdots$O hydrogen bond in the current complex is slightly weaker than these, judging from the distances, but is equally linear. Even in the disordered structure, it likely offers a significant contribution to the stability of the crystal.

A comparison of the solution and solid state structures is informative, and infrared studies on the materials reported above are useful. TEMPO-H exhibits two strong infrared resonances at 3411 and 3448 cm^{-1}. These bands disappear in all the reactions with the carbenes. The reaction product formed from TEMPO-H and IMes is soluble in hexanes, and in C_6D_6 solution evidence of a hydrogen bonded complex is suggested by the observation of O–*H* and N–*C*–N signals in the ^{1}H and ^{13}C NMR spectra, respectively. The reaction product formed between TEMPO-H and SIPr is also soluble in hexanes. Evidence of proton transfer is observed in solution, where C–*H* and N–*C*(H)–N signals are observed in the ^{1}H and ^{13}C NMR (C_6D_6) spectra, respectively. We were unable to crystallize this product but solid samples exhibit a stretch in the infrared spectrum at 3378 cm^{-1}, which is suggestive of a hydrogen bonded complex. Lastly, the product formed from the reaction of BHT and SIPr is soluble in hexanes, and in C_6D_6 solution evidence of the formation of a discrete salt is observed. The anticipated C–*H* and N–*C*(H)–N signals are detected in the ^{1}H and ^{13}C NMR spectra, respectively. In addition, an O–H stretch was not observed in the infrared spectrum.

The difference in the reactivity of TEMPO-H with IMes *vs.* SiPr is dramatic. In the former case, a neutral (O–H$\cdots$C hydrogen bonded) adduct is formed, while in the latter case, proton transfer occurs and an ionic product is recovered. It is difficult to deconvolute the various contributions that give rise

to such differing reactivity. It is likely that steric factors, and π-acceptor effects and σ-donor abilities of the carbenes, all combine to produce the results observed experimentally.

To investigate the reactivity of *N*-heterocyclic carbenes with TEMPO, one equivalent of TEMPO was allowed to react with 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene. No evidence of a reaction was observed in the ^{1}H NMR or infrared spectra of the solids isolated. It has recently been established that much more reactive transient radicals are required for reactions with NHCs such as IMes.[23] Likewise, reaction mixtures of IMes and TEMPO in hexane solutions under a pressure of 5 atm of H_2 did not result in any reaction, as monitored by infrared spectroscopy.



Scheme 5 Reaction of Ph_3PCCO with TEMPO-H.

Lastly, we have examined the reactivity of TEMPO-H with (triphenylphosphoranylidene)ketene (**8**), a molecule that can be viewed as a low-valent carbon source.[24,25] The *C*-centre in this molecule can potentially hydrogen bond,[26] and we were unsure of how it would react with TEMPO-H. The treatment of **8** in anhydrous CH_2Cl_2 with one equivalent of **1** (Scheme 5) resulted in the formation of a clear solution. ^{31}P NMR studies on the reaction mixture indicated the formation of a single species (19 ppm). After the solvent was removed, a light pink-coloured solid was obtained. ^{1}H NMR studies in $CDCl_3$ solutions indicated the presence of both a Ph_3P fragment as well as the TEMPO moiety. The solid had a sharp melting point and its elemental analysis was consistent with a 1 : 1 addition product between TEMPO-H and **8**. Notable from the IR data was a strong peak at 1644 cm^{-1}, consistent with a C═O moiety in the product. An X-ray structural determination was performed on the crystals, the results of which are shown in Fig. 5.

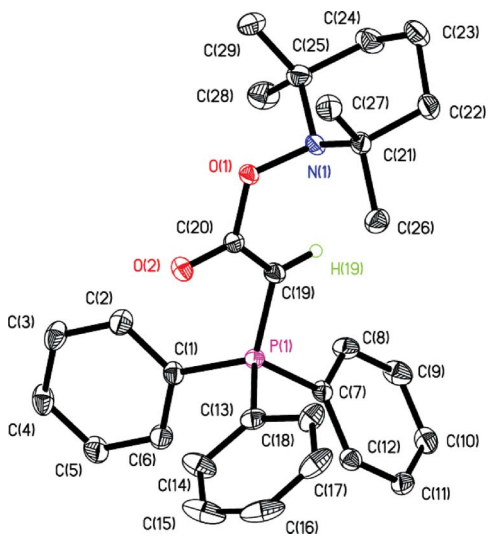


Fig. 5 Crystal structure (50% probability ellipsoids) of the TEMPO–C(═O)C(H)P(Ph)$_3$ molecule.

The molecule can be thought of in two parts, the TEMPO and PCCO regions, joined by a O_{TEMPO}–C_{PCCO} bond. The geometry of the TEMPO fragment can be compared to the structures of anhydrous TEMPO-H (this work), hydrated TEMPO-H (Mader *et al.*[10]) and the free TEMPO radical (Yonekuta *et al.*[13]). The TEMPO fragment of this molecule has a geometry similar to those of TEMPO-H and hydrated TEMPO-H, and is quite different from that of the TEMPO radical. In particular, the N–O bond length of 1.4562(15) Å is similar to those reported in TEMPO-H (1.459(2) Å average, this work) and in hydrated TEMPO-H (1.456(6) average).[10] However, it is quite different from that in TEMPO (1.284(8) Å),[13] since the latter bond is shortened by a significant π contribution. This is also reflected in the C–N–C (119.32(11)°) and C–N–O (106.65(10) and 106.17(10)°) bond angles in the molecule, which are similar to those in TEMPO-H and hydrated TEMPO-H, but which are again quite different from those in the TEMPO radical[13] (C–N–C (123.7(6)°) and C–N–O (114.9(6) and 116.8(5)°), where the bond angles are affected by the π contribution in the NO bond.

The TEMPO part of the molecule is joined to the PCCO part by an O–C bond that is 1.3944(16) Å, slightly shorter than a typical C–O single bond (1.43 Å).[27] The slightly decreased bond length undoubtedly occurs because of the interaction with the PCCO fragment of the molecule. There are a number of related PCCO-type complexes reported in the literature, for example $Ph_3PCHCOPh$[28] and $Ph_3PC(COMe)(COPh)$.[29] In these complexes, the authors describe the PCCO unit as being best thought of as a combination of three resonance contributors, the ylene (P═C), the ylide (P^+–C^-) and the enolate (charge separation on P^+ and O^-). The geometries of the complexes they report are echoed in the PCCO portion of the current molecule.

The geometry around the central P1 atom is nearly tetrahedral. The P1–C19 bond, with a length of 1.7075(14) Å, is shorter than the other P–C_{phenyl} bonds (average 1.8079(15) Å) in the molecule, which suggests it possesses partial double bond character. The C20–O2 bond is longer (1.2315(17) Å) than an average C═O bond length (1.210 Å),[27] while the C19–C20 bond (1.4046(19) Å) is also longer than a typical C═C bond (1.331 Å).[27] These bond lengths support the idea of resonance delocalization occurring in the molecule. Atoms C19 and C20 have distorted trigonal planar geometries (P1–C19–C20 = 116.19(11)°, C19–C20–O1 = 120.89(13)° and C19–C20–O2 = 126.32(13)°), suggesting an sp^2-type hybridization for these carbon atoms, in keeping with the resonance delocalized model.

H(19), the hydrogen atom in the central portion of the PCCO fragment, was refined isotropically to give a C19–H19 bond length of 0.966(18) Å. It did not participate in any hydrogen bonding-type interactions and, in fact, no hydrogen bonds, stacking interactions or other intermolecular interactions of any importance were noted.

The atoms in the central region of the molecule, including P1, C19, C20, O2, O1 and N1, can be used to define a plane. The mean deviation of these atoms from the plane is only 0.0611 Å and the largest deviation from the plane is –0.1046 Å for C19 (H19 lies –0.1285 Å from the defined plane). As suggested by Kalyanasundari *et al.*,[28] this planarity also supports the resonance delocalization model. It is reflected again in the torsion angles for this region of the molecule, P1–C19–C20–O1 = 175.35(10)°, P1–C19–C20–O2 = –6.3(2)°, C19–C20–O1–N1 = –10.72(18)° and

O2–C20–O1–N1 = 170.70(11)°, all values similar to those reported by Spencer *et al.*[29] and Kalyanasundari *et al*.[28]

The non-bonded distance between P1 and O2 is 2.94 Å, significantly less than the sum of the van der Waals radii for phosphorus and oxygen (3.3 Å).[30] As described by both Spencer *et al.*[29] and Kalyanasundari *et al.*,[26] this suggests that there is a strong intramolecular interaction between the P^+ and O^- charge centres of the enolate resonance contributor, which in turn leads to the molecule adopting a *cis* orientation.

Conclusions

In summary, we have reported a reliable preparation for anhydrous TEMPO-H and fully characterized this product. We have demonstrated the utility of anhydrous TEMPO-H *vs.* the hydrated form, both in terms of greater stability during synthesis and differing reactivity patterns. We have described the reactions of TEMPO-H with a number of low-valent *C*-containing materials. Anhydrous TEMPO-H is much more stable than its hydrated form, and reacts in a variety of modes with low-valent carbon sites.

Experimental

General experimental

An argon atmosphere double manifold vacuum line and argon atmosphere dry box (mBraun Unilab) were used for the manipulation of air- and moisture-sensitive compounds. Ultra-high purity argon gas was used in all cases. Anhydrous solvents were available directly using an mBraun MB-SPS solvent purification system. All melting points were determined using a Barnstead Mel-Temp apparatus. NMR spectra were obtained using Bruker Avance 500 MHz and/or AC-250 spectrometers. IR spectra were obtained using a Bruker Vertex 70 infrared spectrometer as either potassium bromide pellets or as dichloromethane solutions between potassium bromide plates. Elemental analyses were performed using a Perkin-Elmer CHN analyzer.

NMR spectra were obtained at the Nuclear Magnetic Resonance Research Resource (NMR-3), Dalhousie University, Halifax, Canada. ^{1}H and ^{13}C spectral shifts are reported in relation to either known residual solvent peaks or TMS, when available. ^{31}P spectral shifts were taken without internal calibration.

Synthetic methods

Preparation of anhydrous 1-hydroxy-2,2,6,6-tetramethyl-piperidine (TEMPO-H) in two steps

Preparation of sodium 2,2,6,6-tetramethyl-piperidine-1-oxide. In a 300 mL sealable Schlenk-type reaction vessel, 0.46 g (20 mmol) of Na metal was heated until molten. Through slow rotation of the vessel as the metal cooled, a sodium mirror was deposited on the flask wall and allowed to harden *via* slow cooling to ambient temperature. 3.12 g (20 mmol) of commercially available 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO) and 100 mL of dry hexanes were added and the mixture brought to reflux at 70 °C for 12 h. The solution underwent an observable change overnight from the characteristic deep red of TEMPO to a brown solution with a light precipitate. After reduction of the solvent by 50%, the suspension was filtered and the remaining volatiles removed under reduced pressure, yielding a light grey powder. Yield: 2.91 g (83.3%).

Preparation of anhydrous 1-hydroxy-2,2,6,6-tetramethyl-piperidine (TEMPO-H). In a 500 mL Schlenk flask 2.91 g (0.0163 mol) of sodium 2,2,6,6-tetramethyl-piperidine-1-oxide was added to a suspension of 2.18 g (0.0163 mol) of triethylamine hydrochloride in 100 mL of dry Et_2O. The reaction was allowed to proceed for 12 h, at which point the solution was filtered through a vacuum frit with a Celite® bed to remove excess reagents and any sodium salts produced. Removal of the Et_2O and triethylamine *in vacuo* yielded pure anhydrous 1-hydroxy-2,2,6,6-tetramethyl-piperidine (TEMPO-H). Single crystals were grown at –35 °C by sublimation of the material onto the side of a sealed vial. Yield: 1.39 g (54%). mp 35–36 °C. ^{1}H NMR (250 MHz, C_6D_6) δ: 8.36 (s, 1 H, NO*H*), 2.35 (br m, 18 H, $^3J_{H-H}$ = 7 Hz, CH_3, CH_2). ^{13}C{^{1}H} NMR (250 MHz, C_6D_6) δ: 128.7, 128.3, 127.9, 59.1, 39.9, 26.6, 17.6. IR (KBr, cm^{-1}) μ: 3478 (m), 3411 (m), 2972 (s), 2934 (s), 1468 (m), 1421 (w), 1380 (m), 1360 (m), 1293 (m), 1262 (m), 1240 (w), 1207 (w), 1183 (m), 1135 (m), 1045 (m), 997 (w), 957 (m), 872 (w), 783 (m), 684 (m), 582 (m), 506 (m). Anal. calc. for $C_9H_{19}NO$: C, 68.74; H, 12.18; N, 8.91. Found: C, 68.45; H, 12.40; N, 9.08%.

Synthesis of $[CHNC_6H_2(CH_3)_3]_2C \cdots HO(NC_5H_6(CH_3)_4)$

To a solution of 100.0 mg (0.33 mmol) of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene in hexanes, 51.9 mg (0.33 mmol) of anhydrous 1-hydroxy-2,2,6,6-tetramethyl-piperidine was added. Filtration through a Celite® plug followed by slow evaporation of the remaining solvent yielded X-ray quality crystals. Yield: 82 mg (0.177 mmol, 54%). mp 86–89 °C. ^{1}H NMR (250 MHz, C_6D_6) δ: 8.38 (br s, 1 H, NO*H*), 7.75 (s, 2 H, Ar-*H*), 7.34 (s, 2 H, Ar-*H*), 5.33 (s, 2 H, NC*H*), 3.10 (s, 18 H, Ar–CH_3), 2.32 (br s, 6 H, CH_2), 1.98 (br s, 12 H, CCH_3). ^{13}C{^{1}H} NMR (250 MHz, C_6D_6) δ: 210.9, 138.0, 137.1, 135.0, 128.7, 128.3, 127.9, 120.3, 57.5, 39.7, 26.0, 20.7, 19.6. IR (KBr, cm^{-1}) μ: 3124 (m), 2988 (s), 2968 (s), 2920 (s), 2770 (m), 1642 (w), 1609 (w), 1542 (w), 1489 (s), 1444 (s), 1388 (s), 1350 (m), 1293 (w), 1251 (s), 1208 (w), 1181 (w), 1131 (m), 1084 (m), 1034 (m), 959 (m), 926 (m), 854 (s), 783 (w), 723 (m), 665 (w), 633 (w), 573 (w), 510 (w). Anal. calc. for $C_{30}H_{43}N_3O$, C, 78.05; H, 9.39; N, 9.10. Found C, 77.89; H, 9.45; N, 9.11%.

Synthesis of $[CH_2N\textit{i}\text{-}Pr_2C_6H_3]_2CH \cdots O(NC_5H_6(CH_3)_4)$

To a solution of 100.0 mg (0.255 mmol) of 1,3-bis(2,6-diiso-propylphenyl)imidazolidin-2-ylidene in hexanes, 40.0 mg (0.255 mmol) of anhydrous 1-hydroxy-2,2,6,6-tetramethyl-piperidine was added. No crystalline product was isolated after multiple attempts; the solid was characterized by spectroscopic methods. Yield: 122 mg (0.223 mmol, 87%). mp 112–115 °C. ^{1}H NMR (250 MHz, C_6D_6) δ: 9.17 (s, 1 H, NC*H*), 8.10–7.89 (m, 6 H, Ar–H), 4.80 (t, 2 H, $^3J_{H-H}$ = 7 Hz, NCH_2), 4.57 (t, 2 H, $^3J_{H-H}$ = 7 Hz, N′C′H_2), 4.32 (sept, 1 H, $^3J_{H-H}$ = 7 Hz, CH(CH$_3$)$_2$), 4.13 (sept, 2 H, $^3J_{H-H}$ = 7 Hz, C′H(CH$_3$)$_2$), 3.96 (sept, 1 H, $^3J_{H-H}$ = 7 Hz, C″H(CH$_3$)$_2$), 2.19 (br m, 18 H, (CH_3)$_2$CCH_2CH_2CH_2C(CH_3)$_2$, 2.00 (d, 12 H, $^3J_{H-H}$ = 7 Hz, CHCH_3), 1.89 (d, 12 H, $^3J_{H-H}$ = 7 Hz, C′HCH_3). ^{13}C{^{1}H} NMR (250 MHz, C_6D_6) δ: 163.1, 147.6, 142.1, 136.0, 128.7, 127.3, 127.9, 124.2. 123.8, 123.5, 49.5, 48.7,

28.1, 27.7, 25.0, 24.1, 23.1. IR (KBr, cm^{-1}) μ: 3378 (w), 3068 (w), 2964 (s), 2930 (m), 2869 (m), 1660 (s), 1624 (m), 1463 (s), 1411 (m), 1384 (m), 1362 (m), 1301 (m), 1262 (m), 1236 (m), 1191 (m), 1097 (w), 1055 (w), 993 (w), 868 (w), 845 (m), 756 (m), 578 (w), 510 (w). Anal. calc. for $C_{36}H_{57}N_3O$, C, 78.92; H, 10.49; N, 7.67. Found, C, 78.15; H, 10.24; N, 7.29%.

Synthesis of $[CH_2N\ i\text{-}Pr_2C_6H_3]_2CH\cdots OC_6H_2CH_3(C(CH_3)_3)_2$

To a solution of 100.0 mg (0.26 mmol) of 1,3-bis(2,6-diisopropylphenyl)-imidazolidin-2-ylidene in hexanes, 57.3 mg (0.26 mmol) of butylated hydroxytoluene (BHT) was added. After filtration of the solution through a Celite® plug, slow evaporation of solvent yielded X-ray quality yellow crystals. Yield: 127 mg (0.208 mmol, 80%). mp 134–136 °C. ^{1}H NMR (250 MHz, C_6D_6) δ: 9.17 (s, 1 H, NC*H*), 8.25–8.00 (m, 8 H, Ar-*H*), 4.81 (t, 2 H, $^3J_{H-H}$ = 7 Hz, NCH_2), 4.63 (t, 2 H, $^3J_{H-H}$ = 7 Hz, N′C′H_2), 4.23 (sept, 4 H, $^3J_{H-H}$ = 7 Hz, CH(CH$_3$)$_2$), 3.19 (s, 3 H, Ar–CH_3), 2.33 (s, 18 H, C(CH_3)$_3$), 1.89–2.30 (m, 24 H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (250 MHz, C_6D_6) δ: 163.1, 151.7, 146.9, 135.6, 128.7, 128.3, 127.9, 125.4, 123.6, 53.3, 33.9, 30.1, 28.6, 25.0, 24.1, 23.3, 21.1. IR (KBr, cm^{-1}) μ: 2961 (s), 2717 (w), 2617 (w), 2370 (w), 1658 (w), 1606 (m), 1583 (s), 1462 (s), 1421 (s), 1386 (m), 1311 (m), 1262 (m), 1192 (w), 1101 (w), 1051 (w), 1018 (w), 991 (w), 802 (m), 754 (m), 579 (w). Anal. calc. for $C_{42}H_{62}N_2O$ C, 82.57; H, 10.23; N, 4.59. Found C, 81.98; H, 10.39; N, 4.23%.

Synthesis of $Ph_3PC(H)C(=O)O(NC_5H_6(CH_3)_4)$

To a solution of 302 mg (1 mmol) (triphenylphosphoranylidene)ketene in anhydrous dichloromethane, 157 mg (1 mmol) of anhydrous 1-hydroxyl-2,2,6,6-tetramethyl-piperidine was added. The solution was stirred and slow evaporation of the solvent yielded light pink, X-ray quality crystals. Yield: 403 mg (0.87 mmol, 87%). mp. 163–166 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.68 (m, 6 H, Ar-*H*), 7.55 (m, 3 H, Ar-*H*), 7.47 (m, 6 H, Ar-*H*), 3.61 (br s, 1 H, C*H*), 1.58 (m, 5 H, CH_2), 1.38 (m, 1 H, CH_2), 1.24 (m, 12 H, CH_3). ^{13}C-NMR (500 MHz, CD_2Cl_2) δ: 133.2, 131.9, 128.8, 128.0, 60.0, 40.0, 32.6, 20.6, 17.4. ^{31}P (500 MHz, CD_2Cl_2) δ: 19.4. IR (NaCl salt plate, cm^{-1}): μ: 3027 (s), 2975 (s), 2924 (s), 2871 (s), 2102 (w), 1944 (w), 1860 (w), 1806 (w), 1644 (m), 1605 (s, C═O), 1494 (s), 1461 (m), 1439 (m), 1356 (m), 1333 (m), 1265 (s), 1183 (w), 1107 (m), 1085 (m), 1030 (w), 932 (w), 893 (s), 732 (s), 696 (s), 552 (w), 520 (w).

Theoretical calculations

Calculations were performed using Gaussian 03[31] and a stepping stone approach, in which the geometries at the levels HF/STO-3G, HF/3-21G, HF/6-31G*, HF/6-31+G* and B3LYP/6-31+G* were sequentially optimized using default specifications. After each level, a frequency calculation was performed to verify the nature of the stationary point. *Z*-matrix coordinates constrained to the appropriate symmetry were used for efficiency, as any problems would manifest themselves by an imaginary mode orthogonal to the spanned *Z*-matrix space. The Hessian was also evaluated at the starting STO-3G geometry to aid convergence. Only the B3LYP/6-31+G* results are reported.

General data collection and refinement details

A summary of crystallographic data for the studied compounds is shown in Table 3. Data was collected on a Bruker Smart diffractometer running APEX2[32] software, with Mo-Kα radiation

Table 3 Crystallographic data for the reported compounds

Identification code	Anhydrous TEMPO-H	Unsaturated IMes⋯ TEMPO-H	Saturated SIPr⋯ BHT	$Ph_3PC(H)C(=O)ON$-$(C_5H_6(CH_3)_4)$
Empirical formula	$C_9H_{19}NO$	$C_{30}H_{43}N_3O$	$C_{42}H_{62}N_2O$	$C_{29}H_{34}NO_2P$
Formula weight	157.25	461.67	610.94	459.54
T/K	100(2)	100(2)	100(2)	296(2)
Size/mm^3	0.31 × 0.29 × 0.27	0.23 × 0.19 × 0.18	0.30 × 0.21 × 0.20	0.40 × 0.37 × 0.22
Crystal system	Trigonal	Monoclinic	Orthorhombic	Monoclinic
Space group	$R\bar{3}$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
a/Å	18.7761(16)	10.989(2)	10.2181(7)	11.9030(13)
b/Å	18.7761(16)	15.262(3)	19.3153(14)	12.1631(13)
c/Å	43.329(4)	16.648(4)	19.5555(14)	18.100(2)
α (°)	90	90	90	90
β (°)	90	94.250(3)	90	93.6420(10)
γ (°)	120	90	90	90
Volume/Å^3	13229(2)	2784.5(10)	3859.6(5)	2615.1(5)
Z	54	4	4	4
Density (calculated)/Mg m^{-3}	1.066	1.101	1.051	1.167
Absorption coefficient/mm^{-1}	0.068	0.067	0.061	0.130
Reflections collected	21413	22240	42693	20480
Independent reflections	5195	6707	4462	6326
R_{int}	0.0471	0.0392	0.1297	0.0492
Max. and min. transmission	0.7459 and 0.6486	0.7458 and 0.6662	0.9877 and 0.9819	0.7457 and 0.6680
Data/restraints/parameters	5195/0/322	6707/0/311	4462/393/549	6326/0/30
Goodness-of-fit on F2	1.096	1.025	0.956	1.020
Final R indices [$I > 2\sigma(I)$] $R1$	0.0420	0.0475	0.0438	0.0419
Final R indices [$I > 2\sigma(I)$] w$R2$	0.0861	0.1140	0.0945	0.1017
R indices (all data) $R1$	0.0781	0.0695	0.0675	0.0591
R indices (all data) w$R2$	0.0993	0.1271	0.1026	0.1133
Largest differential peak and hole/e Å^{-3}	0.200 and –0.199	0.273 and –0.247	0.204 and –0.158	0.448 and –0.286

(0.71073 Å) and ω scans. A temperature of 100(2) K was used for data collection, except for the TEMPO–Ph_3PCCO complex, where the data was collected at room temperature. Data was corrected for absorption effects using the multi-scan method (SADABS[32]). Cell refinement and data reduction were carried out using the SAINT[32] program. Structures were solved by direct methods (SHELXS-97[33]) and refined on F^2 by full-matrix least-squares (SHELXL-97[33]). Hydrogen atoms were placed in calculated positions with a riding refinement, except for those involved in hydrogen bonding, which were refined freely and isotropically. The remaining H atoms were placed in geometrically idealized positions and were allowed to ride on the parent C atom with $U_{iso(H)} = 1.2U_{eq(C)}$ or $U_{iso(H)} = 1.5U_{eq(C)}$ for the idealized methyl protons.

The structure of the complex formed when the unsaturated NHC was protonated with BHT, $[CH_2N\textit{i}\text{-}Pr_2C_6H_3]_2CH\cdots OC_6H_2CH_3(C(CH_3)_3)_2$, proved to be highly disordered. To solve the disorder, a variety of restraints and constraints had to be applied during the refinement. Bond lengths and angles were restrained to geometrically reasonable distances using a combination of SADI and DFIX commands. In order to obtain satisfactory thermal parameters, SIMU and ISOR restraints were applied to some of the disordered atoms. A short contact remains in the final refined structure, H23C$\cdots$H41F. It is believed to arise from the disorder present in the crystal and from the atoms being brought into close proximity by the strong C–H$\cdots$O hydrogen bond also present in the structure.

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