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Allowing the direct interaction of *N*-aryl α-diimines with a high valent metal chloride: one-pot WCl_6-promoted formation of quinoxalinium salts†

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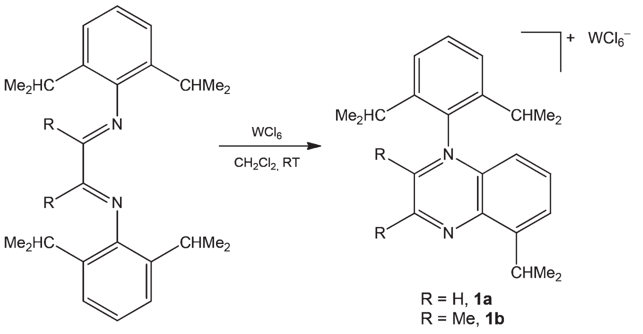
The full potential of a high valent metal chloride as both a chlorinating and an oxidative agent was explored by allowing WCl_6 to react with *N*-(2,6-diisopropylphenyl) α-diimines, in CH_2Cl_2 at room temperature. These α-diimines underwent unprecedented conversion to quinoxalinium cations *via* intramolecular C–N coupling.

α-Diimines (also called 1,4-diaza-1,3-dienes = DAD) constitute a fascinating class of compounds whose steric and electronic properties may be finely tuned by varying the substituents on the N═CC═N skeleton.[1] Due to their versatility and robustness, α-diimines have been widely employed as ancillary chelating ligands in coordination chemistry,[2] assisting a variety of stoichiometric and catalytic transformations.[3] α-Diimines are prone to undergoing a stepwise reduction (up to two electron reduction),[1c,4] and for this reason they are considered as redox non-innocent ligands when bound to a metal centre,[2b,5] possibly determining some ambiguity in the assignment of the oxidation states.[6] On the other hand, the oxidation chemistry of α-diimines still remains, surprisingly, an almost unknown field. As a matter of fact, the electro-oxidation behaviour of non coordinated α-diimines has not been clearly assessed hitherto.[7] Besides, the reactivity studies with high valent metal compounds (oxidation state of the metal ≥4), that are potential, strong oxidizing agents, are exceedingly rare in the literature.[4,8] With reference to homoleptic, high valent transition metal chlorides, the reactivity of $NbCl_5$,[9] $TaCl_5$,[10] $MoCl_5$ [11] and WCl_6 [12] with α-diimines has aroused a recent and notable consideration. However, all the described reactions have been performed with prior reduction, by one or two electrons, of the metal centre. This strategy quenches the activation ability of the strongly acidic metal chlorides,[13–15] so to straightforwardly afford coordination compounds with intact, redox active α-diimine ligands. A similar outcome has been achieved by allowing TiX_4 (X = Cl, Br)[2d,16] and MCl_5 (M = Nb, Ta)[16a,17] to react with dilithium(1,4-diaza-1,3-dienyl) salts.

Herein, we describe for the first time the reactions of two α-diimines with a high valent metal chloride, in a weakly coordinating solvent (dichloromethane) and in the absence of further reactants (*e.g.*, reductants). Thus the 1 : 1 molar reaction of WCl_6 with *N*,*N*′-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (DAD^{Dip}) afforded the quinoxalinium salt $[\{2,6\text{-}C_6H_3(CHMe_2)_2\}N(CH)_2NCC(CHMe_2)(CH)_3C][WCl_6]$, **1a**, in 60% yield (Scheme 1).[18] Compound **1a** was isolated and then characterized by spectroscopic methods and single crystal X-ray diffraction (see Fig. 1, and Table SI1 in the ESI†). The analogous **1b** was obtained in 45% yield from WCl_6 and 2,3-bis(2,6-diisopropylphenylimino) butane (Me-DAD^{Dip}), see Scheme 1.

Significant amounts of isopropyl chloride were clearly recognized by NMR/GC-MS analyses on the liquids distilled



Scheme 1 α-Diimine to quinoxalinium conversion promoted by WCl_6.

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† Electronic supplementary information (ESI) available: Details of experimental procedures (including Scheme SI1), X-ray crystallography, electrochemical studies (including Table SI3 and Fig. SI1), computational studies (including Scheme SI2 and Fig. SI2–SI6), NMR spectra (Fig. SI7–SI12). CCDC 1551416 (**1a**·CH_2Cl_2) and 1551419 (**2b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt03226a

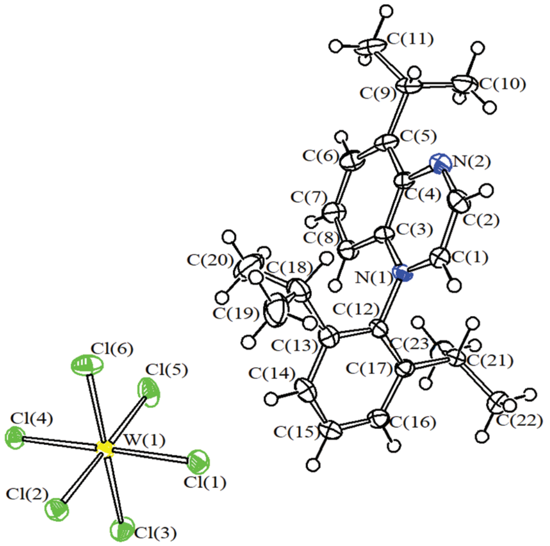


Fig. 1 View of the structure of **1a** with key atoms labeled. Displacement ellipsoids are at the 50% probability level. Only one of the two independent cation–ion pair present within the unit cell is represented.

from the $WCl_6/DAD^{Dip}/CD_2Cl_2$ and WCl_6/Me-DAD^{Dip}/CD_2Cl_2 reaction systems, respectively. By using the same method, we detected limited amounts of alkyl halides as produced from the combination of WCl_6 with some other *N*-aryl α-diimines (see Experimental for details), suggesting that the activation process observed for DAD^{Dip} and Me-DAD^{Dip} might hold some general character.

The crystal structure of **1a** consists in an ionic packing of $[WCl_6]^-$ anions[19] and $[\{2,6\text{-}C_6H_3(CHMe_2)_2\}N(CH)_2NCC(CHMe_2)(CH)_3C]^+$ cations. The bonding parameters of the quinoxalinium core do not significantly differ from those previously reported for *N*-alkyl-quinoxalium cations.[20] Quinoxalinium salts have aroused interest as possible chemosensors,[21] in synthetic organic chemistry[22] and for their pharmaceutical[23] and photophysical properties.[24] They are usually generated *via* the condensation of α-diketones with 1,2-phenylenediamines.[24a,25a,b,26] A restricted number of *N*-aryl quinoxalinium salts have been synthesized to date,[25b,27] and the crystallographic characterization of **1a** provides the first X-ray structure of a *N*-aryl-quinoxalium cation ever reported. It should be remarked here that the known activation reactions of α-diimines are rare,[5c,28] being usually limited to C–C and C–Cl coupling additions to the imine carbons.[9,10,28–30] A tricyclic dipyrrolopyrrole was obtained by $FeCl_2$-promoted oligomerization of a *N*-aryl α-diimine, accompanied by the loss of half of one DAD fragment.[31] The cyclization reaction presented herein has more affinity with the chemistry of 2,3-bis(diphenylphosphino)-1,4-diazadienes, undergoing a peripheral ring closure upon coordination of the phosphine groups to group 10 metal halides.[32]

Several experiments, including electrochemical analyses and spectroscopic studies, and DFT calculations allowed to elucidate some mechanistic aspects of the WCl_6 promoted cyclization reaction of DAD^{Dip}.

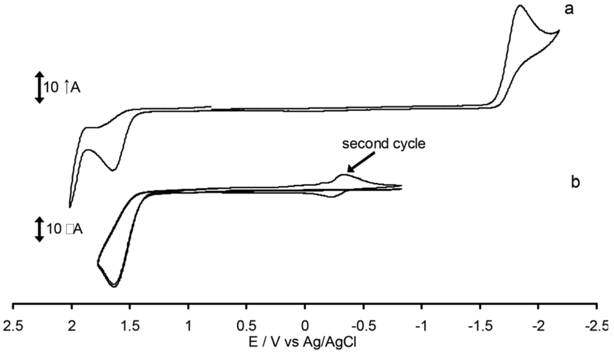
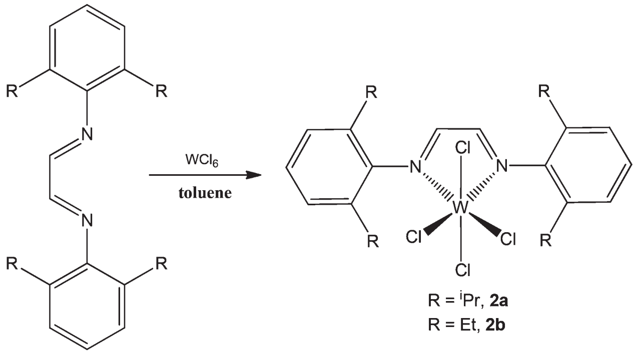


Fig. 2 Cyclic voltammograms of DAD^{Dip} recorded at a Pt electrode in CH_2Cl_2 solution containing $[^nBu_4N][PF_6]$ 0.2 M. Scan rate 0.1 V s^{-1}. (a) Cyclic voltammetry obtained starting the scan toward negative potentials from +0.8 V; (b) 2 cycles voltammetry between −0.8 and 1.8 V.

First, the voltammetric investigation of a series of α-diimines (see Chart 1 in the ESI† and Fig. 2 for DAD^{Dip}) at a Pt disk electrode was performed in CH_2Cl_2. The examined compounds underwent, in addition to the well established one-electron reduction, an oxidation process at potentials ranging between 1.43 and 1.70 V.[33] These values would allow, in principle, a chemical oxidation by WCl_6 in CH_2Cl_2 ($E^{\circ\prime}$ *ca.* 1.6 V *vs.* Ag/AgCl/KCl).[34]

Notwithstanding, variable temperature EPR analysis of a WCl_6/DAD^{Dip} mixture in CH_2Cl_2 did not allow to detect any trace of $[DAD^{Dip}]^+$. Otherwise, the electrochemical oxidation of DAD^{Dip} to $[DAD^{Dip}]^+$ did not lead to final formation of the quinoxalinium cation contained in **1a** (see comparison of UV spectra in Fig. SI1†). Accordingly, the reaction in CH_2Cl_2 of DAD^{Dip} with $NOBF_4$, *i.e.* a typical oxidizing agent whose power is comparable to that of WCl_6,[34] did not give the quinoxalinium derivative among a complicated mixture of products. These facts suggest that the synthesis of **1a**, albeit containing a W(V) anion, cannot be the consequence of a simple electron transfer from DAD^{Dip} to W(VI). In agreement with these experimental observations, key intermediates along a plausible reaction pathway to **1a** were DFT calculated (see Scheme SI2 and Fig. SI2–SI6†).

On theoretical grounds, it appears that the initial interaction WCl_6–DAD^{Dip} results in a favourable Cl-attack to one of the two C=N moieties (Fig. SI2 and SI3†). Experimentally, the 1 : 1 reaction in CD_2Cl_2 of DAD^{Dip} with PCl_5, *i.e.* a typical chlorinating substance employed in organic synthesis,[35] selectively proceeded with H/Cl substitution at one imine group to give $[\{2,6\text{-}C_6H_3(CHMe_2)_2\}N{=}CHC(Cl){=}N\{2,6\text{-}C_6H_3(CHMe_2)_2\}]$ as the stable product (Scheme SI1†). Following chlorination of the organic substrate, one-electron transfer from the newly formed ligand to the metal centre is likely to occur. This step is concomitant with the migration of one chloride from the metal to isopropyl-substituted carbon atom. The cyclization step should then take place favoured by the presence of both an activated aromatic ring and a formally anionic nitrogen atom. The release of isopropyl chloride (see above) is likely to represent the driving force for the entire process. The radical



Scheme 2 Synthesis of W(IV) coordination complexes from WCl_6 and α-diimines in toluene.

Table 1 Selected bond distances (Å) and angles (°) for **2b**

W(1)–Cl(1)	2.351(3)	W(1)–Cl(2)	2.349(3)
W(1)–Cl(3)	2.296(3)	W(1)–Cl(4)	2.250(3)
W(1)–N(1)	2.032(10)	W(1)–N(2)	2.054(9)
N(1)–C(1)	1.344(15)	N(2)–C(2)	1.351(15)
C(1)–C(2)	1.381(17)		
Cl(1)–W(1)–Cl(2)	169.60(11)	Cl(3)–W(1)–N(1)	161.7(3)
Cl(4)–W(1)–N(2)	160.9(3)	Cl(3)–W(1)–Cl(4)	110.88(12)
N(1)–W(1)–N(2)	73.7(4)	W(1)–N(1)–C(1)	120.1(8)
N(1)–C(1)–C(2)	113.4(11)	C(1)–C(2)–N(2)	113.3(10)
C(2)–N(2)–W(1)	118.9(8)		

derived from isopropyl elimination (Fig. SI6†) could be oxidized to the final quinoxalinium cation either by WCl_5 ($\Delta G = -7.5$ kcal mol^{-1}) or more easily by still unreacted WCl_6 ($\Delta G = -40.8$ kcal mol^{-1}).

The W(IV) coordination complex $WCl_4(DAD^{Dip})$, **2a**,[12a] was identified as a side-product in the synthesis of **1a**. The solvent polarity revealed to be crucial in regulating the **1a**/**2a** ratio (see ESI, page S13†). In fact, when toluene was employed as the reaction medium in the place of dichloromethane, **2a** became the major product (60% yield, Scheme 2). It is noticeable that this method may provide an alternative route to $W^{IV}Cl_4(DAD)$ coordination complexes, in the absence of a Cl-abstracting agent.[12a] We found that the reaction of WCl_6 with DAD^{Det} in toluene afforded the W(IV) complex **2b** in 40% yield (Scheme 2).

The new compound **2b** was characterized by analytical and spectroscopic techniques, and by X-ray diffraction (Fig. 3, Table 1). The structure of **2b** resembles that previously reported for **2a**.[12a]

In summary, the unusual, *direct interaction* of *N*-aryl α-diimines, *i.e.* widely employed robust ligands in coordination chemistry, with a high valent metal chloride has provided the unprecedented one-pot conversion to quinoxalinium species, *via* C_{aryl}–C_{alkyl} bond activation and subsequent intramolecular C–N coupling. Based on experimental and computational outcomes, the most probable reaction pathway exploits the rather unique synergic properties offered by WCl_6,[13] acting as both a powerful chlorinating species[13,36] and a strong oxidant.[19,34,37] We are currently working to develop this concept in the direction to achieve unconventional transformations of suitable organic substrates.

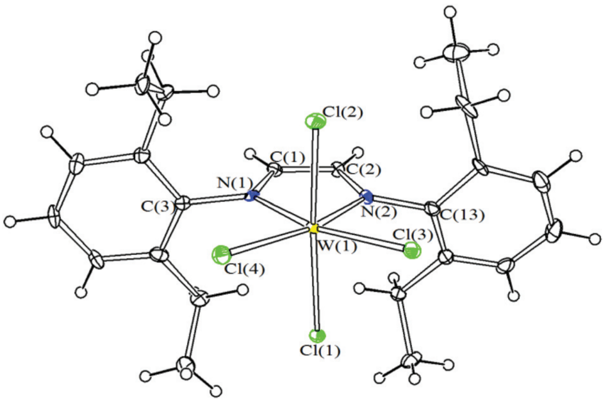


Fig. 3 View of the structure of **2b** with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 (*a*) A. Raghavan and A. Venugopal, *J. Coord. Chem.*, 2014, **67**, 2530–2549; (*b*) L. Guo, H. Gao, Q. Guan, H. Hu, J. Deng, J. Liu, F. Liu and Q. Wu, *Organometallics*, 2012, **31**, 6054–6062; (*c*) E. Uhlig, *Pure Appl. Chem.*, 1988, **60**, 1235–1240; (*d*) G. Van Koten and K. Vrieze, *Adv. Organomet. Chem.*, 1982, **21**, 151–239.

2 Selected references are: (*a*) T. Chu, Y. Boyko, I. Korobkov, L. G. Kuzmina, J. A. K. Howard and G. I. Nikonov, *Inorg. Chem.*, 2016, **55**, 9099–9104; (*b*) R. E. Rodrìguez-Lugo, M. Trincado, M. Vogt, F. Tewes, G. Santiso-Quinones and H. Grützmacher, *Nat. Chem.*, 2013, **5**, 342–347; (*c*) M. Ma, A. Stasch and C. Jones, *Chem. – Eur. J.*, 2012, **18**, 10669–10676; (*d*) T. Spaniel, H. Görls and J. Scholz, *Angew. Chem., Int. Ed.*, 1998, **37**, 1862–1865; (*e*) K. Mashima, Y. Matsuo and K. Tani, *Organometallics*, 1999, **18**, 1471–1481.

3 Selected references are: (*a*) I. Pappas, S. Treacy and P. J. Chirik, *ACS Catal.*, 2016, **6**, 4105–4109; (*b*) W. N. Palmer, J. V. Obligacion, I. Pappas and P. J. Chirik, *J. Am. Chem. Soc.*, 2016, **138**, 766–769; (*c*) R. Wang, X. Sui, W. Pang and C. Chen, *ChemCatChem*, 2016, **8**, 434–440; (*d*) J. L. Rhinehart, N. E. Mitchell and B. K. Long, *ACS Catal.*, 2014, **4**, 2501–2504; (*e*) M. S. Winston, P. F. Oblad, J. A. Labinger and J. E. Bercaw, *Angew. Chem., Int. Ed.*, 2012, **51**, 9822–9824; (*f*) C. Chen, S. Luo and R. F. Jordan, *J. Am. Chem. Soc.*, 2010, **132**, 5273–5284.

4 J. Scholz, B. Richter, R. Goddard and C. Krüger, *Chem. Ber.*, 1993, **126**, 57–61.

5 (*a*) X. Wang, Y. Zhao, S. Gong, B. Liu, Q. S. Li, J. H. Su, B. Wu and X. J. Yang, *Chem. – Eur. J.*, 2015, **21**, 13302–13310; (*b*) B. E. Cole, J. P. Wolbach, W. J. Dougherty Jr., N. A. Piro, W. S. Kassel and C. R. Graves, *Inorg. Chem.*, 2014, **53**, 3899–3906; (*c*) J. Li, K. Zhang, H. Huang, A. Yu, H. Hu, H. Cui and C. Cui, *Organometallics*, 2013, **32**, 1630–1635; (*d*) C. Mealli, A. Ienco, A. D. Phillips and A. Galindo, *Eur. J. Inorg. Chem.*, 2007, 2556–2568; (*e*) P. J. Daff, M. Etienne, B. Donnadieu, S. Z. Knottenbelt and J. E. McGrady, *J. Am. Chem. Soc.*, 2002, **124**, 3818–3819.

6 (*a*) K. Takao, S. Tsushima, T. Ogura, T. Tsubomura and Y. Ikeda, *Inorg. Chem.*, 2014, **53**, 5772–5780; (*b*) C. J. Allan, B. F. T. Cooper, H. J. Cowley, J. M. Rawson and C. L. B. Macdonald, *Chem. – Eur. J.*, 2013, **19**, 14470–14483.

7 Studies on the electrochemical reduction of non coordinated α-diimines have been reported, see for instance ref. 6*b* and (*a*) B. G. Shestakov, T. V. Mahrova, J. Larionova, J. Long, A. V. Cherkasov, G. K. Fukin, K. A. Lyssenko, W. C. Scherer, T. V. Magdesieva, O. A. Levitskiy and A. A. Trifonov, *Organometallics*, 2015, **34**, 1177–1185; (*b*) D. A. Matveev, E. F. Sagitova, P. B. Kraykivskii, S. K. Petrovskii, N. S. Gurinovich and V. C. Saraev, *Russ. J. Electrochem.*, 2014, **50**, 239–242.

8 (*a*) K. Dreisch, C. Andersson and C. Stålhandske, *Polyhedron*, 1993, **12**, 1335–1343; (*b*) K. Dreisch, C. Andersson and C. Stålhandske, *Polyhedron*, 1993, **12**, 303–311.

9 H. Nishiyama, H. Ikeda, T. Saito, B. Kriegel, H. Tsurugi, J. Arnold and K. Mashima, *J. Am. Chem. Soc.*, 2017, **139**, 6494–6505.

10 H. Tsurugi, T. Saito, H. Tanahashi, J. Arnold and K. Mashima, *J. Am. Chem. Soc.*, 2011, **133**, 18673–18683.

11 Y. Zhao, Y. Xue, W. Xu, J. H. Su, B. Wu and X.-J. Yang, *Eur. J. Inorg. Chem.*, 2016, 5411–5417.

12 (*a*) H. Tsurugi, H. Tanahashi, H. Nishiyama, W. Fegler, T. Saito, A. Sauer, J. Okuda and K. Mashima, *J. Am. Chem. Soc.*, 2013, **135**, 5986–5989; (*b*) A. J. L. Pombeiro and M. F. N. N. Carvalho, *Rev. Port. Quim.*, 1981, **23**, 23–32.

13 (*a*) M. Schubert, P. Franzmann, A. W. von Leupoldt, K. Koszinowski, K. Heinze and S. R. Waldvogel, *Angew. Chem., Int. Ed.*, 2016, **55**, 1156–1159; (*b*) S. R. Waldvogel and S. Trosien, *Chem. Commun.*, 2012, **48**, 9109–9119.

14 M. Bortoluzzi, T. Funaioli, F. Marchetti, G. Pampaloni, C. Pinzino and S. Zacchini, *Chem. Commun.*, 2017, **53**, 364–367.

15 (*a*) Y. Satoh and Y. Obora, *Eur. J. Org. Chem.*, 2015, 5041–5054; (*b*) T. Toda, N. Nakata, T. Matsuo and A. Ishii, *ACS Catal.*, 2013, **3**, 1764–1767; (*c*) K. Fuchibe, T. Kaneko, K. Mori and T. Akiyama, *Angew. Chem., Int. Ed.*, 2009, **48**, 8070–8073.

16 (*a*) B. Richter, J. Scholz, J. Sieler and K.-H. Thiele, *Angew. Chem., Int. Ed.*, 1996, **34**, 2649–2651; (*b*) J. Scholz and H. Görls, *Polyhedron*, 2002, **21**, 305–312.

17 H. Tom Dieck, H. J. Rieger and G. Fendesak, *Inorg. Chim. Acta*, 1990, **177**, 191–197.

18 The use of 2 : 1 or 1 : 2 W/diimine stoichiometry led to a decrease of the reaction yield.

19 M. Bortoluzzi, F. Marchetti, G. Pampaloni, C. Pinzino and S. Zacchini, *Inorg. Chem.*, 2016, **55**, 887–893.

20 (*a*) S. I. Gorelsky, A. B. Ilyukhin, P. V. Kholin, V. Y. Kotov, B. V. Lokshin and N. V. Sapoletova, *Inorg. Chim. Acta*, 2007, **360**, 2573–2582; (*b*) U. Siemeling, S. Tomm and C. Bruhn, *J. Organomet. Chem.*, 2006, **691**, 5056–5059; (*c*) K. Woźniak and T. M. Krygowski, *J. Mol. Struct.*, 1989, **193**, 81–92; (*d*) H. J. Keller, D. Nöthe and M. Werner, *Can. J. Chem.*, 1979, **57**, 1033–1036.

21 M. Ishtiaq, I. Munir, M. al-Rashida, A. Maria, K. Ayub, J. Iqbal, R. Ludwig, K. M. Khan, S. A. Ali and A. Hameed, *RSC Adv.*, 2016, **6**, 64009–64018.

22 (*a*) K. Sendil and B. Oezguen, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2006, **181**, 959–964; (*b*) M. S. Kim and S. B. Lee, *Materials*, 2014, **7**, 5581–5590; (*c*) N. Değirmenbaş and B. Özgün, *Monatsh. Chem.*, 2002, **133**, 1417–1421.

23 J. Guillon, M. Boulouard, V. Lisowski, S. Stiebing, V. Lelong, P. Dallemagne and S. Rault, *J. Pharm. Pharmacol.*, 2000, **52**, 1369–1375.

24 (*a*) B. Laramee-Milette, J. G. Ferreira and G. S. Hanan, *ChemistrySelect*, 2017, **2**, 3952–3958; (*b*) S. Kundu, A. Banerjee, A. De, A. Y. Khan, G. S. Kumar, R. Bhadra and P. Ghosh, *J. Fluoresc.*, 2015, **25**, 1645–1654; (*c*) S. Matsumoto, H. Abe and M. Akazome, *J. Org. Chem.*, 2013, **78**, 2397–2404; (*d*) C. A. Roeschlaub, N. L. Maidwell, R. M. Reza and P. G. Sammes, *Chem. Commun.*, 1999, 1637–1638.

25 (*a*) Y. V. D. Nageswar, K. H. V. Reddy, K. Ramesh and S. N. Murthy, *Org. Prep. Proced. Int.*, 2013, **45**, 1–27; (*b*) S. Gobec and U. Urleb, Science of Synthesis, in *Quinoxalines*, ed. Y. Yamamoto and I. Shinkai, 2004, pp. 845–911.

26 C. Delpivo, G. Micheletti and C. Boga, *Synthesis*, 2013, 1546–1552.

27 (*a*) D. Schelz, *Helv. Chim. Acta*, 1978, **61**, 2452–2462; (*b*) D. Schelz and M. Priester, *Helv. Chim. Acta*, 1975, **58**, 317–320.

28 F. S. Mair, R. Manning, R. G. Pritchard and J. E. Warren, *Chem. Commun.*, 2001, 1136–1137.

29 A. Hinchliffe, F. S. Mair, E. J. L. McInnes, R. G. Pritchard and J. E. Warren, *Dalton Trans.*, 2008, 222–233.

30 A. A. Trifonov, E. A. Fedorova, G. K. Fukin, N. O. Druzhkov and M. N. Bochkarev, *Angew. Chem., Int. Ed.*, 2004, **43**, 5045–5048.

31 I. E. Buys, S. Elgafi, L. D. Field, T. W. Hambley and B. A. Messerle, *Inorg. Chem.*, 1994, **33**, 1539–1542.

32 (*a*) D. Walther, S. Liesicke, L. Böttcher, R. Fischer, H. Görls and G. Vaughan, *Inorg. Chem.*, 2003, **42**, 625–632; (*b*) D. Walther, S. Liesicke, R. Fischer, H. Görls, J. Weston and A. Batista, *Eur. J. Inorg. Chem.*, 2003, 4321–4331.

33 The electrochemical oxidation of α-diimines is complicated by a subsequent, fast transformation of the presumably generated radical cation, as pointed out by the appearance,

in the second scan toward negative potentials of a 2 cycles voltammetric experiment, of a reduction peak at −0.33 V.

34 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.

35 (*a*) D. Hua, P. Yang, Y. Shen, G. Yang and Z. Chai, *Tetrahedron*, 2017, **73**, 1205–1210; (*b*) J. E. Burks Jr., *Phosphorus(v) Chloride in Encyclopedia of Reagents for Organic Synthesis*, 2001; (*c*) T. Onak, L. B. Friedman, J. A. Hartsuck and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1966, **88**, 3439–3440.

36 M. Bortoluzzi, F. Marchetti, M. G. Murrali, G. Pampaloni and S. Zacchini, *Dalton Trans*, 2015, 44, 8729–8738.

37 M. Bortoluzzi, F. Marchetti, G. Pampaloni and S. Zacchini, *Chem. Commun.*, 2015, **51**, 1323–1325.