469, 221; c) A. L. Casalnuovo, J. C. Calabresse, D. Milstein, J. Am. Chem. Soc. **1988**, *110*, 6738; d) R. Dorta, P. Egli, F. Zürcher, A. Togni, *J. Am. Chem. Soc.* **1997**, *119*, 10857; e) M. A. Giardello, V. P. Conticello, L. Bard, M. R. Gagné, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10241; f) Y. Li, T. J. Marks, J. Am. Chem. Soc. **1996**, *118*, 9295; g) Y. Li, T. J. Marks, *Organometallics* **1996**, *15*, 3770; h) A. L. Seligson, W. C. Trogler, *Organometallics* **1993**, *12*, 744, and references therein.

[3] B. de Bruin, M. J. Boerakker, J. J. J. M. Donners, B. E. C. Christiaans, P. P. J. Schlebos, R. de Gelder, J. J. M. Smits, A. L. Spek, A. W. Gal, *Angew. Chem.* **1997**, 109, 2153; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2064.

[4] The few isolated 2-metallaoxetanes known are all stabilized by various substituents. Consequently, it is difficult to deduce the intrinsic reactivity of the unsubstituted 2-metallaoxetane moiety from these substituted examples: a) V. W. Day, W. G. Klemperer, S. P. Lockledge, D. J. Main, *J. Am. Chem. Soc.* **1990**, *112*, 2031; b) A. A. Zlota, F. Frolow, D. Milstein, *J. Am. Chem. Soc.* **1990**, *112*, 6411; c) M. J. Calhorda, A. M. Galvão, C. Ünaleroglu, A. A. Zlota, F. Frolow, D. Milstein, *Organometallics* **1993**, *12*, 3316; d) D. P. Klein, J. C. Hayes, R. G. Bergman, *J. Am. Chem. Soc.* **1988**, *110*, 3704; e) J. C. Hartwig, R. G. Bergman, R. A. Andersen, *Organometallics* **1991**, *10*, 3344; f) J. C. Hartwig, R. G. Bergman, R. A. Andersen, *J. Am. Chem. Soc.* **1990**, *112*, 3234; g) S. Baba, T. Ogura, S. Kawaguchi, H. Tokunan, Y. Kai, N. Kashi, *J. Chem. Soc. Chem. Commun.* **1972**, 910; h) L. Pandolfo, G. Paiaro, G. Valle, P. Ganis, *Gazz. Chim. Ital.* **1985**, *115*, 65; i) W. A. Herrmann, U. Küsthardt, A. Schäfer, E. Herdtweck, *Angew. Chem.* **1986**, *98*, 818; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 817; j) R. Schlodder, J. A. Ibers, M. Lenarda, M. Graziani, *J. Am. Chem. Soc.* **1974**, *96*, 6893; k) M. Lenarda, N. B. Pahor, M. Calligaris, M. Graziani, L. Randaccio, *J. Chem. Soc. Dalton Trans.* **1978**, 279.

[5] For an overview of 2-metallaoxetane reactivity, see K. A. Jørgensen, B. Schiøtt, *Chem. Rev.* **1990**, *90*, 1483.

[6] Details of the crystal structure determination are available as supporting information on the WWW.

[7] $\delta(CD_3CN) = 4.02$ (t, $^3J(H,H) = 7.4$ Hz; $RhCH_2CH_2O$), 3.27 (dt, $^3J(H,H) = 7.4$ Hz, $^2J(Rh,H) = 2.7$ Hz; $RhCH_2CH_2O$). These signals are similar to those recorded for separately prepared $[(tpa)Rh^{III}$(2-hydroxyethyl)(Cl)]BPh_4: $\delta(CD_3CN) = 3.98$ (t, $^3J(H,H) = 7.9$ Hz; $RhCH_2CH_2O$), 3.16 (dt, $^3J(H,H) = 7.9$ Hz, $^2J(Rh,H) = 2.6$ Hz; $RhCH_2CH_2O$.

[8] For the intramolecular Pinner reaction from $[(PMe_3)_4Ir^{III}(CH_2OH)(N{\equiv}CMe)]^{2+}$ to κ^2-*N*,*C*-2-(acetimidoyloxy)-methyl complex $[(PMe_3)_4Ir^{III}(CH_2OC(Me){=}NH)]^{2+}$, see D. L. Thorn, J. C. Calabrese, *J. Organomet. Chem.* **1984**, *272*, 283. For other examples of nitrile C≡N-bond activation by metal coordination (including Pinner type reactions with alcohols), see B. N. Storhoff, H. C. Lewis Jr., *Coord. Chem. Rev.* **1977**, *23*, 1

[9] For the Pinner syntheses, see J. March, *Advanced Organic Chemistry*, 4th ed, Wiley, **1992**, p. 892, and references therein. For the Ritter reaction, see J. March, *Advanced Organic Chemistry*, 4th ed, Wiley, **1992**, p. 970, and references therein.

[10] Single crystals of $\mathbf{4}\cdot(BPh_4)_2\cdot CH_3CN$ were mounted in air on a glass fibre. Intensity data were collected on an Enraf–Nonius CAD4 diffractometer with graphite monochromatized $Cu_{K\alpha}$ radiation ($\lambda = 1.541838$ Å). Data were collected at room temperature ($\theta-2\theta$ scan mode). Unit cell dimensions were determined from the angular setting of 15 reflections. Intensity data were corrected for Lorentz and polarization effects. A semi-empirical absorption correction (ψ scan)[10a] was applied. The structures were solved by the program system DIRDIF[10b] by using the program PATTY[10c] to locate the heavy atom and were refined with standard methods (refinement against F^2 of all reflections with SHELXL97[10d] with anisotropic parameters for the non-hydrogen atoms. The hydrogen atoms of the methyl groups were refined as rigid rotors with idealized sp^3 hybridization and a C–H bond length of 0.97 Å to match the maximum electron density in a difference Fourier map. The hydrogen atom attached to the nitrogen atom was taken from a difference Fourier map. All other hydrogen atoms were initially placed at calculated positions and were freely refined subsequently. Crystal data ($C_{72}H_{69}B_2N_6ORh$, $M_r = 1158.86$): monoclinic, space group $C2/c$, $a = 28.270(2)$, $b = 23.0952(14)$, $c = 21.520(2)$ Å, $\beta = 119.793(6)°$, $V = 12192.9(16)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.263$ g cm^{-3}; final R indices: $R_1 = 0.0552$ (for 6778 reflections considered observed ($I > 2\sigma(I)$)), $wR_2 = 0.1255$ (all data) for the 993 total variables.[10e] a) A. C. T North, D. C. Philips, F. S. Mathews; *Acta Crystallogr.* **1968**, *A24*, 351; b) P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel, J. M. M. Smits, DIRDIF-96, computer program system for crystal structure determination by Patterson and direct methods applied to difference-structure factors, Crystallography Laboratory, University of Nijmegen (Netherlands), **1996**; c) P. T. Beurskens, G. Beurskens, M. Strumpel, C. E. Nordman in *Patterson and Pattersons* (Eds.: J. P. Glusker, B. K. Patterson, M. Rossi), Clarendon, Oxford, **1987**, p. 356; d) G. M. Sheldrick, SHELXL-97, program for the refinement of crystal structures, Universität Göttingen (Germany), **1997**; e) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101855 and CCDC-101856 for $\mathbf{4}\cdot(BPh_4)_2\cdot MeCN$ and $\mathbf{3}\cdot(BPh_4)_2\cdot MeOH$, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)

[11] a) O Heilmann, H. D. Hausen, W. Kaim, *Z. Naturforsch Teil B* **1994**, *49*, 1554; b) B. McCullogh, J. Halpern, M. R. Thompson, C. R. Landis, *Organometallics* **1990**, *9*, 1392; c) M. Costa, G. P. Chiusoli, F. Salvadori, G. Bocelli, *Gazz. Chim. Ital* **1995**, *125*, 589; d) B. E. Villarroya, L. A. Oro, F. J. Lahoz, A. J. Edwards, M. A. Ciriano, P. A. Alonso, A. Tiripicchio, M. Tiripicchio Camellini, *Inorg. Chim. Acta* **1996**, *250*, 241; e) M. I. Arriortua, J. L. Pizarro, J. Ruiz, J. M. Morena, E. Colacio, *Inorg. Chim. Acta* **1995**, *231*, 103; f) G. Bocelli, G. P. Chiusoli, M. Costa, M. Michelotti, *J. Chem. Soc. Perkin Trans. 1* **1994**, 1347; g) N. W. Alcock, J. M. Brown, P. J. Maddox, *J. Chem. Soc. Chem. Comm.* **1986**, 1532; g) N. W. Alcock, J. M. Brown, A. E. Derome, A. R. Lucy, *J. Chem. Soc. Chem. Comm.* **1985**, 575.

[12] The thermal decomposition of alkylalkanimidates yields, among others, nitriles and alcohols or trisubstituted 1.3.5-triazines and alcohols: a) F. Cramer, K. Pawelzik, J. Kupper, *Angew. Chem.* **1956**, *20*, 649; b) P. Reynaud, R. C. Moreau, *Bull. Soc. Chim. Fr.* **1964**, 2997. See also ref. [13].

[13] F. Cramer, N. Hennrich, *Chem. Ber.* **1961**, 976, and references therein.

Domino Effect in the Buildup of N-I-N-I Chains of the *N*-Iodine(triphenylphosphane)imine

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Bernhard Neumüller, and Kurt Dehnicke*

Nitrogen–iodine compounds are often associated through N-I-N-I chains of the donor–acceptor type. Examples are the iodine–nitrogen derivatives $NI_3\cdot NH_3$[1] and $NI_3\cdot$pyridine,[2] which form polymers, and the iodine azide which is monomeric in the gas phase[3, 4] but forms zigzag chains with the iodine atoms in the solid state through the α-N atoms of the azide groups.[3] The hypervalent character of the iodine atoms in these compounds, which causes the association, reveals itself above all in the ionic derivatives $[I_2N_3]^+[SbF_6]^-$,[5] $[PPh_4]^+[I(N_3)_2]^-$,[6] and in the halide complexes of *N*-iodosuc-

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cinimide $[\text{PPh}_4]^+[\text{X}(\text{INC}_4\text{O}_2\text{H}_4)_2]^-$ (X = Cl, Br, I).[7] On the other hand, *N*-iodine(triphenylphosphane)imine shows no tendency at all towards intermolecular N–I⋯N association in the solid state, although—according to the crystal structure analysis—the nitrogen atom is sp^3-hybridized and shows Lewis basicity, while the iodine atom should be Lewis acidic because of its hypervalent character.[8] We have now found that such an association is initiated, however, if INPPh_3 is allowed to react with elemental iodine. This leads to the formation of the binuclear complex **1** [Eq. (1)] when equimolar quantities of the reactants are applied.

$$2\,\text{INPPh}_3 + 2\,\text{I}_2 \longrightarrow \underset{\mathbf{1}}{[\text{I}(\text{INPPh}_3)_2]^+\text{I}_3^-} \qquad (1)$$

According to the crystal structure analysis,[9] in complex **1** the iodine cation I1, which is formed by redox disproportionation, links the nitrogen atoms of both the INPPh_3 molecules with each other through N-I-N bonds that differ only slightly in length (224.8 and 231.1 pm) (Figure 1). The bond angle at I1 is almost linear (176.1°), which is in agreement with the VSEPR theory[10] (three equatorially arranged lone pairs of electrons at I1). Two of the cations in **1** are connected with the triiodide ions through both the terminal iodine atoms to form a centrosymmetric nonplanar twelve-membered ring (Figure 1). These interionic $\text{I}^{\delta+}\cdots\text{I}_3^-$ distances of 333.3 pm correspond quite well to the I⋯I bond lengths of between 331.5 and 338.5 pm in diorganodiiodonium iodides such as *t*Bu(*i*Pr)-$\text{PI}_2\cdots\text{I}$ and are described as soft–soft interactions.[11]

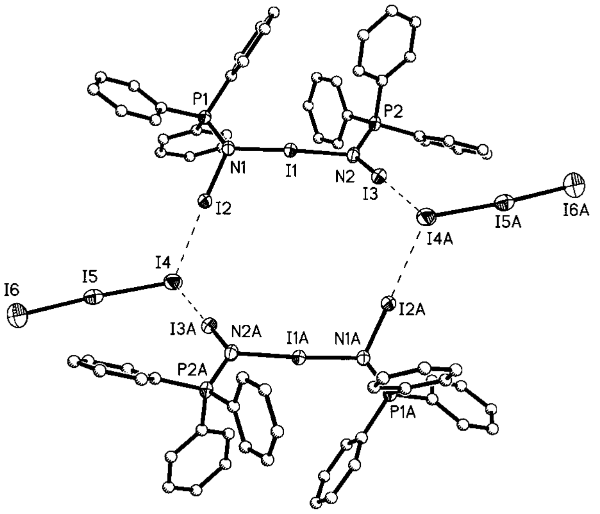


Figure 1. Structure of the dimeric ion pair in **1** in the crystal. Selected bond lengths [pm] and angles [°]: I1–N1 224.8(4), I1–N2 231.1(4), I2–N1 210.4(4), I3–N2 209.1(4), I2–I4 333.3(1), I3–I4A 329.20(6), I4–I5 303.2(1), I5–I6 282.1(1), P–N (av) 162.2; I1-N1-I2 111.2(2), I1-N2-I3 110.9(2), N1-I1-N2 176.1(1), I2-I4-I5 112.52(2), I2-I4-I3A 92.26(2), I3A-I4-I5 91.93(2).

If the amount of iodine applied in Equation (1) is halved, four INPPh_3 molecules can associate to form the tetranuclear complex **2** [Eq. (2)].According to the crystal structure analysis,[9] in the cation of **2** the iodine atoms located at the beginning and at the end are linked by the triiodide ion to form a twelve-membered ring again with C_2 symmetry (Figure 2); the twofold axis runs through the atoms I1 and I5. The support span of the terminal iodine atoms I3 and I3A of the cation allows only a weak interaction with the I_3^- ion as shown by the distances I3⋯I4 of 369.9 pm. However, these distances are still significantly shorter than the van der Waals sum of radii (440 pm). In the cation of **2**, now, the three bridging iodine atoms I1, I2, and I2A have iodonium character with linear functionality. But in the N-I-N-I chain of **2** the distances alternate more strongly than in **1**; the shortest bond of 207.4 pm starts from the quasi-terminal iodine atom I3 and is thus only a little longer than in INPPh_3 (205.6 pm).[8] The short N2–I3 bond in **2** is followed by the long N2–I2 bond (256.1 pm) in the chain, while the two following N–I bonds (212.5 and 226.5 pm) suffer an attenuation in the alternation of distances.

$$4\,\text{INPPh}_3 + 2\,\text{I}_2 \longrightarrow \underset{\mathbf{2}}{[\text{I}(\text{INPPh}_3)_4]^+\text{I}_3^-} \qquad (2)$$

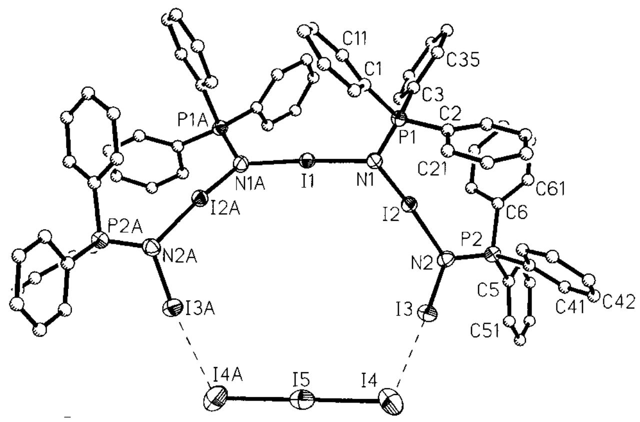


Figure 2. Structure of **2** in the crystal. Selected bond lengths [pm] and angles [°]: I1–N1 226.5(5), I2–N1 212.5(4), I2–N2 256.1(5), I3–N2 207.4(5), I3–I4 369.86(7), I4–I5 289.84(6), P–N (av) 161.1; N1-I1-N1A 176.8(2), N1-I2-N2 175.4(2), I1-N1-I2 115.2(2), I2-N2-I3 105.4(2), N2-I3-I4 166.2(1), I3-I4-I5 102.33(1).

The building block missing between **1** and **2**, that is the linkage of three INPPh_3 molecules, could only be prepared by avoiding formation of triiodide. We achieved this by the complexation of the iodine ion formed according to Equation (3) with the relatively strong electrophile 1,4-diiodotetrafluorobenzene. According to the crystal structure analysis[9]

$$3\,\text{INPPh}_3 + \text{I}_2 + \text{C}_4\text{F}_4\text{I}_2 \longrightarrow \underset{\mathbf{3}}{[\text{I}(\text{INPPh}_3)_3]^+[\text{I}(\text{C}_6\text{F}_4\text{I}_2)]^-} \qquad (3)$$

this electrophile serves as a bridging ligand between symmetry-equivalent iodide ions (Figure 3). Along with the short intermolecular contacts I3⋯F1C (317.8 pm) and I3⋯F2D (323.3 pm), which are shorter than the van der Waals sum of radii by 42 pm and 37 pm, respectively, this leads to a three-dimensional network. It is in the nature of the I⋯I distances between the iodide ion I7 and the iodine atoms of the 1,4-diiodotetrafluorobenzene molecules (339.1 and 342.4 pm) that they are longer than the interionic distance I7⋯I6 to the cation of **3** (309.3 pm). I⋯I distances of 339.8 pm are also found between the iodide ion and diiodoacetylene in $[\textit{cyclo}\text{-C}_3(\text{NMe}_2)_3]^+[\text{I–C}\equiv\text{C–I}\cdots\text{I}]^-$ with a zigzag chain structure in

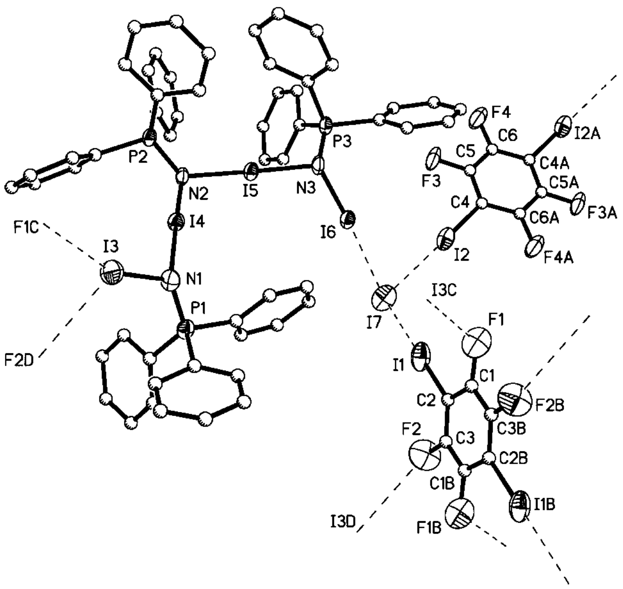
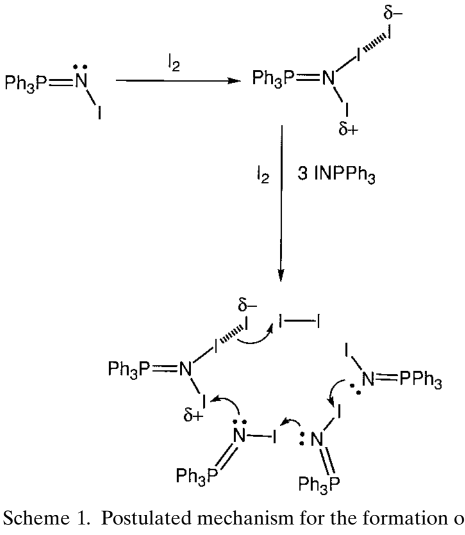


Figure 3. Structure of **3** in the crystal. The ring halves of the $C_6F_4I_2$ molecules that belong to the asymmetric unit are shown completely. Selected bond lengths [pm] and angles [°]: I3–F1A 317.8(10), I3–N1 204.9(9), I4–N1 252.1(9), I4–N2 213.6(8), I5–N2 230.3(8), I5–N3 227.9(8), I6–N3 213.4(9), I6–I7 309.3(2) I2–I7 339.1(2), I1–I7 342.4(2), P–N (av) 160.1; N1-I4-N2 178.3(3), N2-I5-N3 178.2(3), N3-I6-I7 176.7(2), I2-I7-I6 85.43(4), I2-I7-I1B 119.73(4), I6-I7-I1B 108.49(4), I3-N1-I4 110.7(4), I4-N2-I5 110.1(3), I5-N3-I6 116.5(4), C2-I1-I7 173.8(5).

the anion,[12] while the interionic I ··· I distance in the cation of **3** approximately corresponds with the longer I–I bonds in strongly distorted triiodide ions.[13] The structural parameters of the cation of **3** fit in well between those of **1** and **2**. The two iodine atoms I4 and I5 with iodonium character show linear N-I-N bridges, and the chain structure maintains the N-I-N-I alignment with its characteristic alternation of the bond lengths.

The stepwise buildup of the N-I-N chains in **1**–**3** can be understood as a domino mechanism[14] (Scheme 1). For the initiating step one can presume the addition of an iodine molecule to the nitrogen atom of the *N*-iodine(triphenylphosphane)imine. This leads to polarization of the I–I bond in a similar manner to that in crystalline diiodophosphoranes R_3P-I-I.[20] Thus, iodonium character with Lewis acidity is induced at the terminal iodine atom, which again leads to the buildup of a donor–acceptor bond with another $INPPh_3$ molecule and the formation of **1**. This effect continues when further $INPPh_3$ molecules are allowed to react with **1**, the terminal iodine atoms of which also show iodonium character. This process can be controlled by the proportions of the reactants chosen in the reactions (1)–(3). There are indications of a continuation of this domino effect beyond four building blocks, but we could not yet isolate further products.



Scheme 1. Postulated mechanism for the formation of **1**–**3** (for details see text).

Experimental Section

1: A solution of $INPPh_3$[8] (1.08 g, 2.68 mmol) in dichloromethane (30 mL) was added to a solution of iodine (0.68 g, 2.68 mmol) in dichloromethane (80 mL) under stirring. A reddish brown precipitate (1.30 g) was isolated which lost inserted CH_2Cl_2 in vacuo. Cooling the filtrate to −18 °C gave further **1** (0.26 g); total yield 88%. Elemental analysis calcd for $C_{36}H_{30}I_6N_2P_2$ (%): C 32.91, H 2.30, N 2.13; found: C 32.75, H 2.31, N 2.16. Single crystals of $\mathbf{1}\cdot CH_2Cl_2$ were obtained by covering a saturated solution of **1** in dichloromethane with a layer of *n*-hexane and leaving the mixture to stand in the dark.

2: Compound **2** was synthesized by the same procedure as for **1** by using $INPPh_3$ (0.77 g, 1.91 mmol) in dichloromethane (20 mL) and iodine (0.24 g, 0.95 mmol) in dichloromethane (30 mL). After stirring the reaction mixture for 1 d in the dark the orange precipitate was filtrated, washed with a little CH_2Cl_2, and then dried in vacuo; yield 0.88 g (86 %). Elemental analysis calcd for $C_{36}H_{30}I_4N_2P_2$ (%): C 40.78, H 2.85, N 2.64, I 47.88; found: C 40.54, H 2.68, N 2.63, I 47.78.

3: A solution of $INPPh_3$ (0.95 g, 2.36 mmol) in dichloromethane (10 mL) was added to 1,4-diiodotetrafluorobenzene (0.95 g, 2.36 mmol) in dichloromethane (6 mL) and a few mg only of iodine to avoid formation of triiodide. After adding a few drops of *n*-hexane to the reaction mixture, it was allowed to stand for several days at −18 °C. A few orange single crystals were grown and characterized by X-ray diffraction only.

Received: July 31, 1998 [Z12229IE]
German version: *Angew. Chem.* **1999**, *111*, 183–186

Keywords: iodine · oligomers · phosphaneimines

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[1] H. Hartl, H. Bärnighausen, J. Jander, *Z. Anorg. Allg. Chem.* **1968**, *375*, 225.

[2] H. Hartl, D. Ullrich, *Z. Anorg. Allg. Chem.* **1974**, *409*, 228.

[3] P. Buzek, T. M. Klapötke, P. von R. Schleyer, I. C. Tornieporth-Oetting, P. S. White, *Angew. Chem.* **1993**, *105*, 289; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 275.

[4] M. Otto, S. D. Lotz, G. Frenking, *Inorg. Chem.* **1992**, *31*, 3647.

[5] I. C. Tornieporth-Oetting, P. Buzek, P. von R. Schleyer, T. M. Klapötke, *Angew. Chem.* **1992**, *104*, 1391; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1338.

[6] U. Müller, R. Dübgen, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1980**, *468*, 7.

[7] M. Ghassemzadeh, H. Goesmann, D. Fenske, K. Dehnicke, *Z. Naturforsch. B* **1994**, *49*, 602.

[8] J. Grebe, F. Weller, K. Dehnicke, *Z. Naturforsch. B* **1996**, *51*, 1739.

[9] Crystal structure analysis: Enraf-Nonius CAD4 four-circle diffractometer, $Mo_{K\alpha}$ radiation, graphite monochromator, ω scans, temperature 203(2) K, cell determination with 25 reflections, Lorentzian and polarization corrections, direct methods, refinement against F^2, H atoms in calculated positions; calculations performed with: SHELXS-97, SHELXL-97, SHELXTL, PLATON-94, ORTEP. $\mathbf{1}\cdot CH_2Cl_2$: $C_{37}H_{33}Cl_2I_6N_2P_2$, space group $P\bar{1}$, $a = 985.6(1)$, $b = 1346.1(1)$, $c = 1669.8(1)$ pm, $\alpha = 95.99(1)$, $\beta = 94.87(1)$, $\gamma = 97.53(1)°$, $Z = 2$, $V =$

2173.3(3) Å^3, $\rho_{calcd} = 2.139\ g\,cm^{-3}$, $\theta = 2.3-26.0°$. Of 8907 reflections collected, 8523 were independent ($R_{int} = 0.0117$), and 7879 with $I > 2\sigma(I)$, 443 parameters, $R_1 = 0.0326$, wR_2 (all data) = 0.0866. **2**: $C_{72}H_{60}I_8N_4P_4$, space group $C2/c$, $a = 1616.0(1)$, $b = 2493.1(2)$, $c = 1792.1(1)$ pm, $\beta = 96.54(1)°$, $Z = 4$, $V = 7173.1(8)$ Å^3, $\rho_{calcd} = 1.963\ g\,cm^{-3}$, $2\theta = 4.6-50.0°$. Of 6674 reflections collected, 6292 were independent ($R_{int} = 0.0202$), and 5231 with $I > 2\sigma(I)$, 399 parameters, $R_1 = 0.0381$, wR_2 (all data) = 0.0963. **3**: $C_{60}H_{45}F_4I_7N_3P_3$, space group $P\bar{1}$, $a = 933.2(2)$, $b = 1406.6(1)$, $c = 2376.7(2)$ pm, $\alpha = 94.19(1)$, $\beta = 101.15(1)$, $\gamma = 96.89(1)°$, $Z = 2$, $V = 3023.9(7)$ Å^3, $\rho_{calcd} = 2.049\ g\,cm^{-3}$, $\theta = 2.4-25.0°$. Of 11262 reflections collected, 10551 were independent ($R_{int} = 0.0162$), and 8827 with $I > 2\sigma(I)$, 695 parameters, $R_1 = 0.0622$, wR_2 (all data) = 0.1721. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-410019 (**1**), CSD-410020 (**2**), and CSD-410018 (**3**).

[10] R. J. Gillespie, *Angew. Chem.* **1967**, *79*, 885; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 819; R. J. Gillespie, E. A. Robinson, *Angew. Chem.* **1996**, *108*, 539; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 477.

[11] V. Stenzel, J. Jeske, W. W. du Mont, P. G. Jones, *Inorg. Chem.* **1997**, *36*, 443, and references therein.

[12] R. Weiß, M. Rechinger, F. Hampel, A. Wolski, *Angew. Chem.* **1995**, *107*, 483; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 441.

[13] K.-F. Tebbe, in *Rings, Chains and Macromolecules of Main Group Elements* (Ed.: A. L. Rheingold), Elsevier, Amsterdam, **1977**, pp. 551–606.

[14] In recent years domino processes became increasingly important for stereo- and regiocontrolled C–C coupling reactions,[15] in the biosynthesis,[16] for metal-catalyzed syntheses,[17] and in cyclization cascade reactions;[18] cf. also ref. [19]·

[15] T.-L. Ho, *Tandem Organic Reactions*, Wiley-Interscience, New York, **1992**; *Frontiers in Organic Synthesis, Chem. Rev.* **1996**, 96, 1–600; L. F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *105*, 137; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131.

[16] J. K. Sutherland in *Comprehensive Organic Synthesis*, *Vol. 3* (Eds.: B. M. Trost, I. Fleming, G. Pattenden), Pergamon, Oxford, **1991**, p. 341.

[17] P. Canonne, R. Boulanger, M. Bernatchez, *Tetrahedron Lett.* **1987**, *28*, 4997; D. P. Curran in *Comprehensive Organic Synthesis*, *Vol. 4* (Eds.: B. M. Trost, I. Fleming, M F. Semmelhack), Pergamon, Oxford, **1991**, chapter 4.2; H. M. L. Davies, T. J. Clark, H. D. Smith, *J. Org. Chem.* **1991**, *56*, 3817; R. Grigg, P. Kennewell, A. J. Teasdale, *Tetrahedron Lett.* **1992**, *33*, 7789.

[18] A. Padwa, *Chem. Commun.* **1998**, 1417.

[19] E. J. Corey, X. M. Cheng, *The Logic of Chemical Synthesis*, Wiley-Interscience, New York, **1989**, p. 31.

[20] N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard, P. J. Kobryn, *J. Chem. Soc. Dalton Trans.* **1993**, 101; S. M. Godfrey, D. G. Kelly, C. A. McAuliffe, A. G. Mackie, R. G. Pritchard, S. M. Watson, *J. Chem. Soc. Chem. Commun.* **1991**, 1163.

Oxidations of C–H and O–H Bonds by Isolated Copper(III) Complexes**

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Metal-mediated abstractions of hydrogen atoms from C–H and O–H bonds are of interest due to their involvement in metalloenzyme and industrial oxidations. We have shown that metal–oxo complexes oxidize hydrocarbons by a hydrogen-atom abstraction mechanism, which is attributed to their thermodynamic affinity for a hydrogen atom ($\equiv H^+ + e^-$) rather than any radical character within the oxidant.[1] We propose that any metal complex with sufficient affinity for an electron and a proton should exhibit such reactivity. Copper(III) complexes are attracting attention as models for intermediates in copper enzymes such as cytochrome c oxidase and dopamine β-hydroxylase.[2] Proposed catalytic cycles for these and other enzymes involve H-atom abstraction from C–H and/or O–H bonds. Here we report apparent examples of such reactions for two known copper(III) complexes, [Cu(Pre)](ClO$_4$) (**1**-ClO$_4$)[3] and [Cu(H$_{-3}$Aib$_3$)] (**2**).[4] Both complexes are reported to undergo aqueous electrochemical reductions with uptake of one proton [Eq. (1)].

$$Cu^{III}(L) + H^+ + e^- \rightleftarrows Cu^{II}(LH) \qquad (1)$$

[Cu(Pre)]$^+$ (**1**) oxidizes dihydroanthracene (DHA) to anthracene in 60% yield in CH_2Cl_2. To our knowledge, this is the first report of intermolecular hydrocarbon oxidation by an isolable copper(III) complex (Scheme 1). Other workers have reported intramolecular ligand C–H bond oxidation in copper(III) compounds,[5] and Karlin et al. have very recently observed intermolecular C–H bond oxidations in a copper complex + O$_2$ system.[6] The disappearance of **1** in the presence of excess DHA at 20 °C, as monitored by optical spectroscopy in the absence of air or light, followed simple second-order kinetics over several half lives with no apparent induction period [$k_2 = 2.0(\pm 0.1) \times 10^{-3}\,M^{-1}s^{-1}$]. At higher temperatures, the kinetics are increasingly complicated by decomposition of **1** and possibly other reactions. A preliminary Eyring plot (based on k_2 values from 287–328 K) gives $\Delta H^{\neq} \approx 15$ kcal mol^{-1} and $\Delta S^{\neq} \approx -23$ cal K^{-1}mol^{-1}, consistent with a bimolecular rate-determining step (1 cal = 4.184 J). A competition experiment at 55 °C using 9,9′,10,10′-[D$_4$]dihydroanthracene showed a primary kinetic isotope effect of 3.3 ± 0.3. The oxidation of xanthene to bixanthenyl by **1** (detected by GC/MS) is about 10 times faster than DHA oxidation, while reaction with fluorene under similar conditions failed to produce any detectable amounts of 9,9′-bifluorenyl. The relative rates are consistent with the C–H bond strengths (in kcal mol^{-1}) of the substrates: k_2 (xanthene (75.5)) > k_2(DHA (78)) > k_2(fluorene (80)).[7]

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[**] We are grateful to the U.S. National Institutes of Health for financial support, and Professor K. Karlin for helpful comments.