HETEROCYCLES, Vol. 95, No. 2, 2017, pp. 1148-1158. © 2017 The Japan Institute of Heterocyclic Chemistry
Received, 19th October, 2016, Accepted, 25th November, 2016, Published online, 17th February, 2017
DOI: 10.3987/COM-16-S(S)88

SYNTHESIS AND CRYSTAL STRUCTURES OF DICOBALT HEXACARBONYL COMPLEXES OF DICATIONIC ALKYNE-BRIDGED IMIDAZOLIUM AND TRIAZOLIUM DERIVATES

Simone Haslinger,[1] Gerhard Laus,[1] Stefan Oberparleiter,[1] Klaus Wurst,[1] Volker Kahlenberg,[2] Sven Nerdinger,[3]* Erwin Schreiner,[3] and Herwig Schottenberger[1]

[1]Faculty of Chemistry and Pharmacy, Leopold-Franzens University, Innrain 80, 6020 Innsbruck, Austria. [2]Institute of Mineralogy and Petrography, Leopold-Franzens University, Innrain 52, 6020 Innsbruck, Austria. [3]Sandoz GmbH, Biochemiestrasse 10, 6250 Kundl, Austria

Abstract – Dicationic alkyne-bridged imidazolium and triazolium chlorides were subjected to counter-ion replacement reaction with weakly coordinating anions, such as hexafluoridophosphate and bis(trifluoromethanesulfonyl)amide. The resulting low-melting salts were further functionalized to dicobalt hexacarbonyl adducts. Seven crystal structures were determined by X-ray diffraction. Interionic C–H···F and C–H···O contacts were observed.

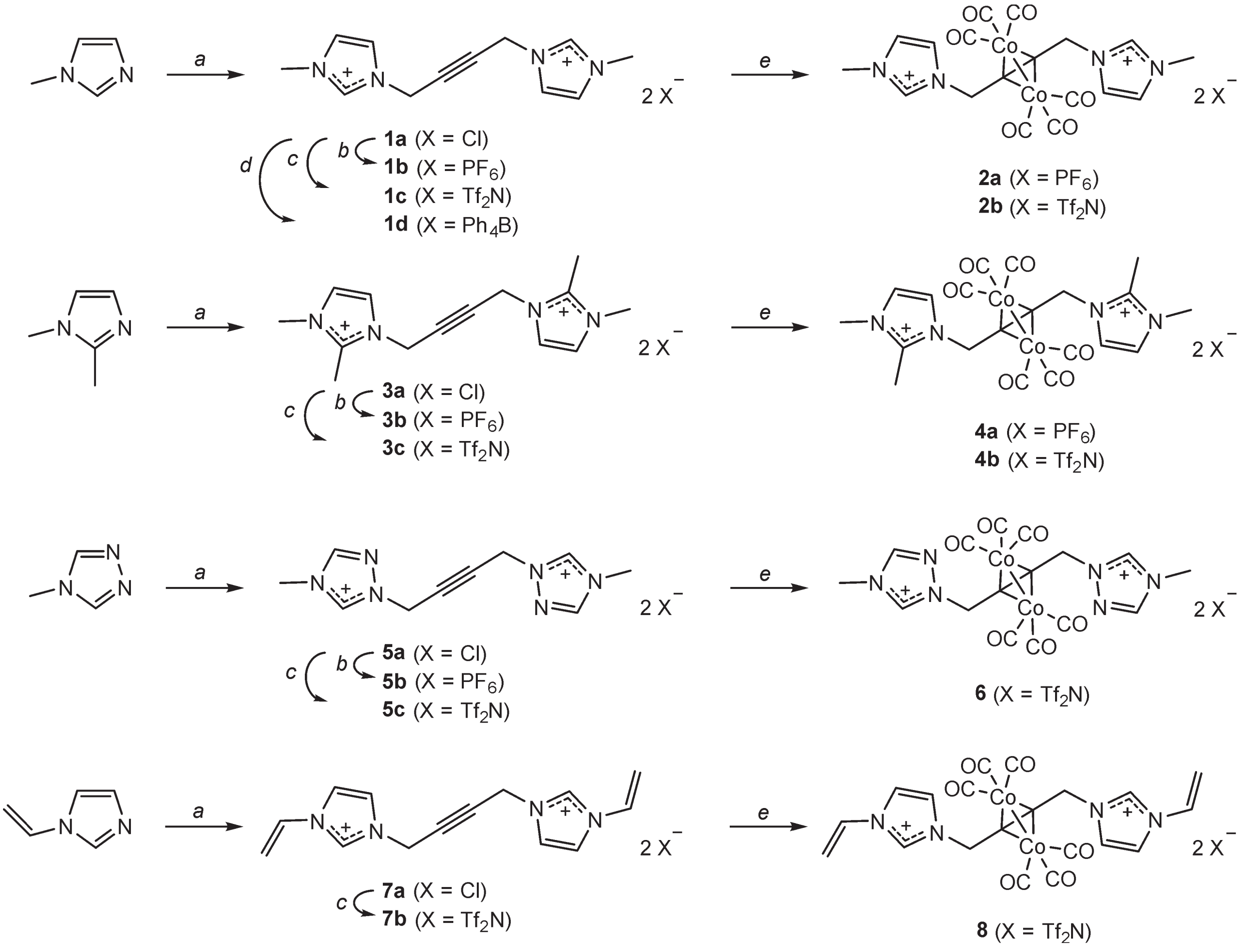
INTRODUCTION

Dicationic imidazolium-based ionic liquids[1] (also called 'gemini imidazolium-based salts')[2] where the heterocyclic systems are bridged by different types of spacers have attained diverse applications. Some of them have been complexed with silver and gold,[3] whereas others have been cross-linked as stationary phases for chromatography.[4] In particular, alkyne-bridged dicationic imidazolium salts[5] appear to be of highest interest. Organometallic complexes derived from alkyne-functionalized imidazolium salts[6] include a new organometallic ionic liquid.[7] Low volatility and restricted leaching in organic solvents are advantageous and desirable properties of these compounds. The synthesis of the first acetylenic dicobalt hexacarbonyl was reported in 1954 in a reaction typical for alkynes.[8,9] Today numerous crystal structures of dicobalt hexacarbonyl complexes are known, but only a very limited number containing imidazole have been reported.[7,10] Therefore, it was our intention to prepare low-melting dicobalt hexacarbonyl complexes of alkyne-bridged dicationic imidazolium salts. 1,2,4-Triazolium salts broaden the scope.

This paper is dedicated to Professor Masakatsu Shibasaki on the occasion of his 70th birthday.

RESULTS AND DISCUSSION

New dicationic alkyne-bridged imidazolium and 1,2,4-triazolium chlorides **1a**, **3a**, **5a** and **7a** were prepared from commercial starting materials. Ion exchange with weakly coordinating anions, such as hexafluoridophosphate and bis(trifluoromethanesulfonyl)amide, yielded low-melting hydrophobic salts **1b**, **3b**, **5b** and **1c**, **3c**, **5c**, **7b** which were further functionalized to dicobalt hexacarbonyl adducts **2a**, **2b**, **4a**, **4b**, **6** and **8** (Scheme 1). Salts with melting points below 100 °C are commonly termed Ionic Liquids (ILs). The bis(trifluoromethanesulfonyl)amides, also referred to as 'bis(triflimides)', **1c** and **5c** are liquid at room temperature. Even dicobalt hexacarbonyl compounds **6** and **8** are classified as ILs. Cobalt carbonyl complexes were obtained in satisfactory yields and characterized by spectroscopic and crystallographic methods. ORTEP plots and packing diagrams with detailed interactions are displayed in Figures 1–7. The dicobalt hexacarbonyl geometry[11] (distances C–C 1.34–1.36 Å and Co–Co 2.45–2.48 Å) is in agreement with that in related compounds (mean values from the Cambridge Structural Database 1.34 and 2.49 Å, respectively).



Scheme 1. *a*: 1,4-dichlorobutyne, MeCN; *b*: NH_4PF_6, H_2O; *c*: $LiTf_2N$, H_2O; *d*: NH_4BPh_4, MeOH; *e*: $Co_2(CO)_8$, THF or CH_2Cl_2

In the crystal structure of **2a** (Figure 1a), two independent molecules of the carbonyl complex are located in the asymmetric unit. Numerous interionic C–H···F contacts are indicated by dashed lines (Figure 1b).

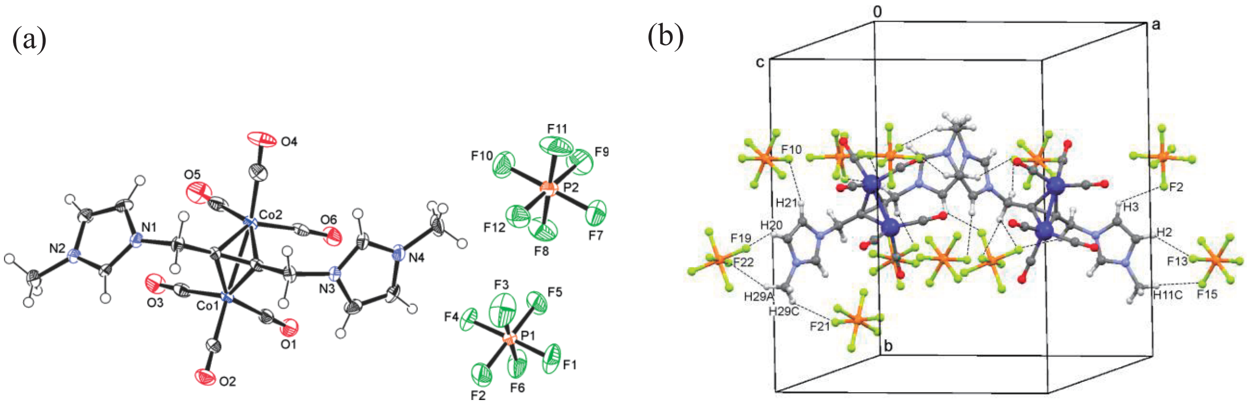


Figure 1. (a) Molecular structure and (b) crystal packing of 3,3'-(2-butyne-1,4-diyl)bis-(1-methylimidazolium) dicobalt hexacarbonyl bis(hexafluoridophosphate) (**2a**)

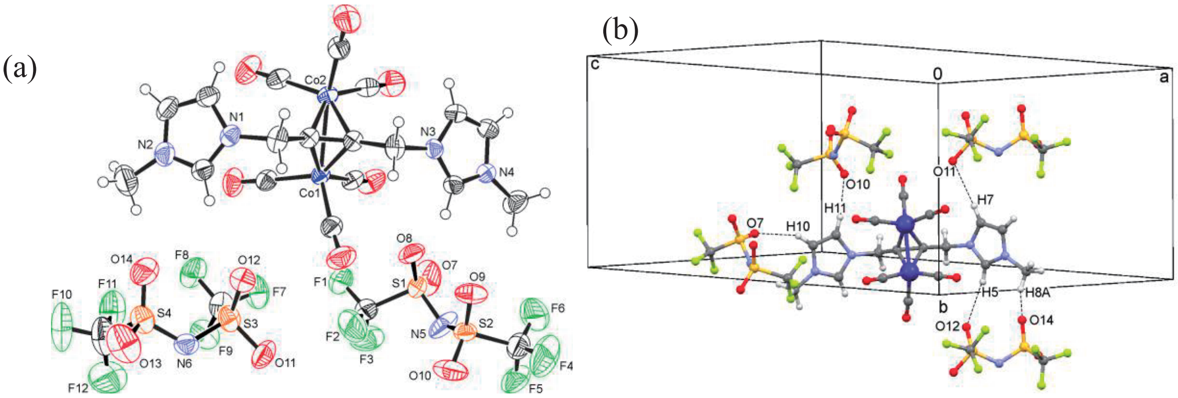


Figure 2. (a) Molecular structure and (b) crystal packing of 3,3'-(2-butyne-1,4-diyl)bis-(1-methylimidazolium) dicobalt hexacarbonyl bis(bis(triflimide)) (**2b**)

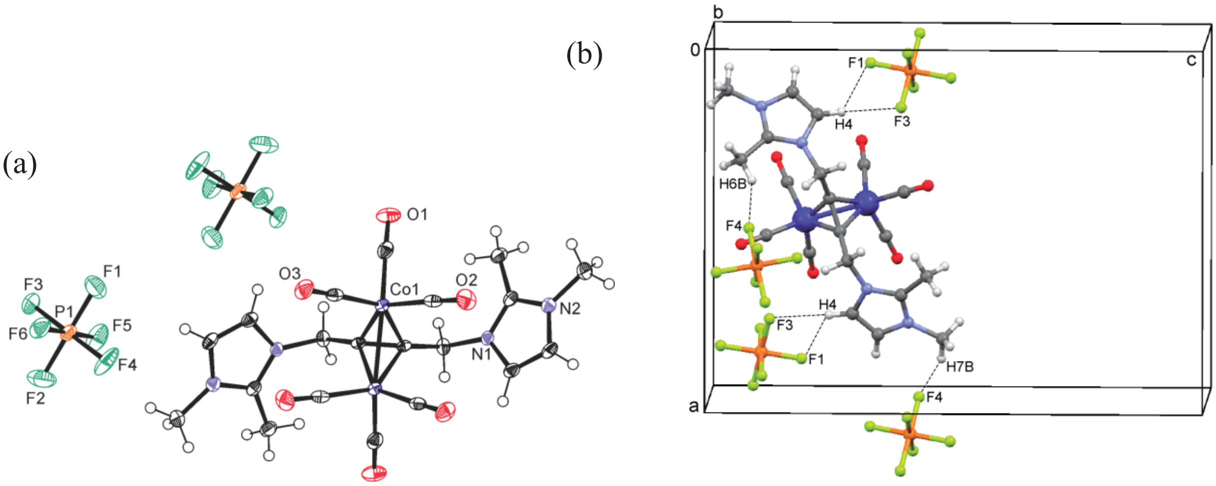


Figure 3. (a) Molecular structure and (b) crystal packing of 3,3'-(2-butyne-1,4-diyl)bis-(1,2-dimethylimidazolium) dicobalt hexacarbonyl bis(hexafluoridophosphate) (**4a**)

Bis(triflimide) anions are known to exist as *syn* or *anti* conformers in the solid state.[12,13] In the crystal structure of **2b**, the anionic molecules adopt both *anti* and *syn* conformations with C–S···S–C torsion angles of 131° and 29° (Figure 2a). Additionally, the *syn* anion exhibits a positional disorder of 25:75. Interionic C–H···O contacts between the aromatic as well as the aliphatic hydrogen atoms and the oxygen atoms of the weakly coordinating bis(triflimide) anions are observed (Figure 2b).

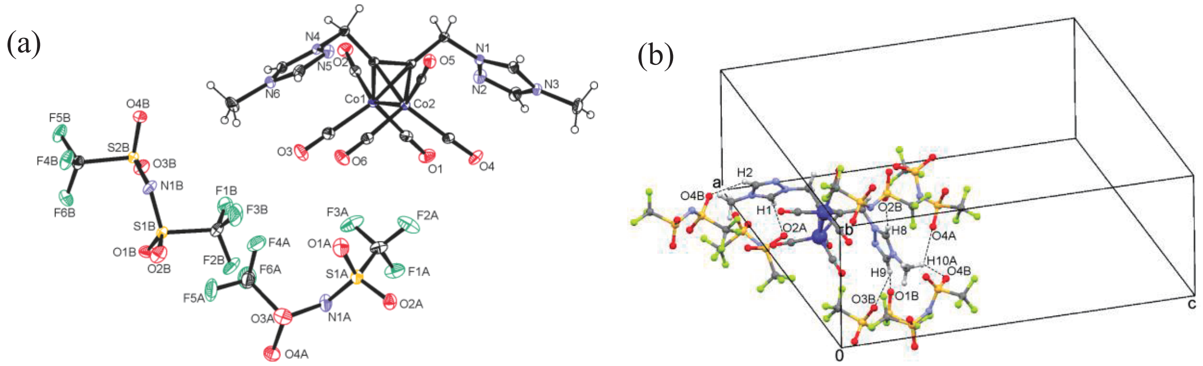


Figure 4. (a) Molecular structure and (b) crystal packing of 1,1'-(2-butyne-1,4-diyl)bis-(4-methyl-1,2,4-triazolium) dicobalt hexacarbonyl bis(bis(triflimide) (**6**)

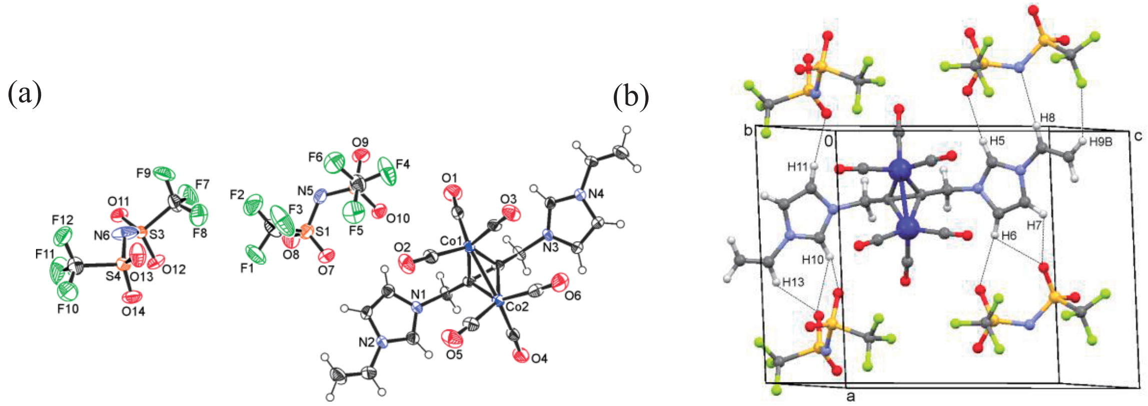


Figure 5. (a) Molecular structure and (b) crystal packing of 3,3'-(2-butyne-1,4-diyl)bis-(1-vinylimidazolium) dicobalt hexacarbonyl bis(bis(triflimide)) (**8**)

In the crystal structure of **4a**, the asymmetric unit contains only half a molecule which is completed by rotation around a two-fold axis parallel to the *b* axis (Figure 3a). A number of short interionic C–H···F contacts are observed (Figure 3b). In **6**, the two bis(triflimide) anions again adopt both *syn* and *anti* conformations with C–S···S–C dihedral angles of 54° and 176°, respectively (Figure 4a). Typically, the bis(triflimide) anions engage in weak C–H···O interactions (Figure 4b). Both kinds of bis(triflimide) conformers, *syn* and *anti*, are found again in the structure of **8** with the pertinent angles of 35° and 134° (Figure 5a), and the ions are connected by C–H···O contacts (Figure 5b). The vinyl groups in **7** and **8** allow for cross-linking by polymerization.

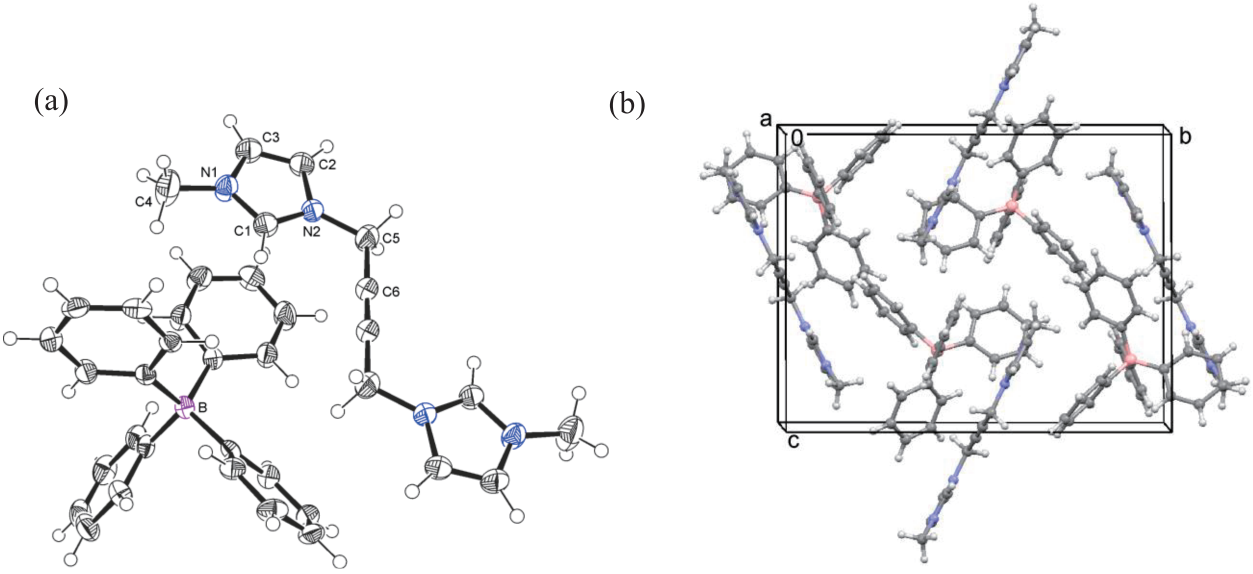


Figure 6. (a) Molecular structure and (b) crystal packing of 3,3'-(2-butyne-1,4-diyl)bis(1-methylimidazolium) bis(tetraphenylborate) (**1d**)

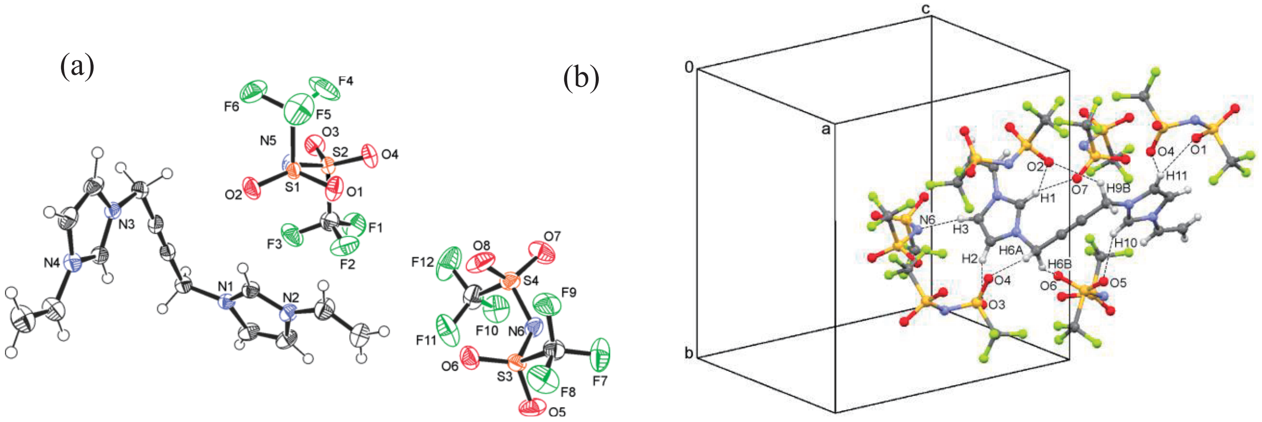


Figure 7. (a) Molecular structure and (b) crystal packing of 3,3'-(2-butyne-1,4-diyl)bis(1-vinylimidazolium) bis(bis(triflimide)) (**7b**)

Other crystal structures determined in the course of this work include the tetraphenylborate **1d** of the bis(1-methylimidazolium) ligand and the known bis(triflimide) **7b** of the bis(1-vinylimidazolium) ligand. Bond angles and lengths of the tetrahedral tetraphenylborate anion are comparable to other reported examples. No directional interactions are observed (Figure 6). In the structure of **7b** both anions adopt *anti* conformations, exhibiting dihedral angles of 176.5° and 176.8° (Figure 7a). Again, weak C–H···O contacts stabilize the framework (Figure 7b).

In summary, a new category of interesting cobalt-containing bidentate ligands with bridged imidazolium or 1,2,4-triazolium systems as potential carbene precursors have been synthesized and characterized. We are planning to develop such materials with NHC-coordinating sites[10] and their metal complexes for electrochemical investigation.

EXPERIMENTAL

Reagents and solvents were purchased from Sigma-Aldrich. NMR spectra were recorded with a Bruker Avance DPX 300 spectrometer. IR spectra were obtained with a Nicolet 5700 FT instrument. Single crystal diffraction intensity data were recorded with Oxford Diffraction Gemini-R Ultra (**1d**, **2a**, **6**, **7b**), NoniusKappa CCD (**2b**) or Bruker D8 (**4a**, **8**) diffractometers using Mo*K*α radiation. Absorption corrections were applied (multi-scan). Structure solution and refinement was performed by direct methods with the programs SIR2002[14] and SHELXL-97.[15] Visualization of the structures and measurements of distances and angles was performed with the programs Ortep-3[16] and Mercury.[17] CCDC 1504029–1504035 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

General procedure for dichlorides. A solution of 1,4-dichloro-2-butyne (1.23 g, 10 mmol) and the respective *N*-alkylazole (20 mmol) in MeCN (15 mL) was stirred at 80 °C for 24 h. The precipitate was collected by filtration, washed with MeCN, and dried under reduced pressure.

General procedure for bis(hexafluoridophosphates). Solutions of the respective chloride (3.5 mmol) in H_2O (2 mL) and ammonium hexafluoridophosphate (1.19 g, 7.3 mmol) in H_2O (2 mL) were combined and stirred for 90 min. The precipitate was filtered off, washed with cold H_2O and dried under reduced pressure.

General procedure for bis(bis(triflimides)). Solutions of the respective chloride (3.5 mmol) in H_2O (5 mL) and lithium bis(triflimide) (2.0 g, 7.0 mmol) in H_2O (5 mL) were combined and stirred for 90 min. The product which precipitated either as a solid or a heavy liquid was washed with H_2O and dried under reduced pressure.

General procedure for dicobalt hexacarbonyl complexes. A solution of the respective alkyne (0.4 mmol) in CH_2Cl_2 (5-10 mL) or THF (5-20 mL) was gassed with Ar for 10 min. Dicobalt octacarbonyl (0.21 g, 0.6 mmol) was added, and the mixture was stirred for 24 h. Then, the solvent was evaporated and the red residue was washed with Et_2O (30 mL) and dried in high vacuum. The resulting oil was stored under Ar at 3 °C and crystallized after several weeks or after the addition of a few drops of CH_2Cl_2.

3,3'-(2-Butyne-1,4-diyl)bis(1-methylimidazolium) dichloride (1a). Yield: 86%, mp 204 °C. IR (neat): ν 3075 (m), 3020 (m), 2946 (w), 2899 (w), 1572 (m), 1558 (m), 1431 (w), 1347 (w), 1179 (s), 1145 (m), 1110 (w), 870 (m), 782 (s), 740 (m), 672 (w), 613 (s) cm^{-1}. For ^1H and ^{13}C NMR spectra see ref. 5.

3,3'-(2-Butyne-1,4-diyl)bis(1-methylimidazolium) bis(hexafluoridophosphate) (1b). Yield: 75%, mp 155 °C. IR (neat): ν 3176 (w), 3130 (w), 1575 (w), 1348 (w), 1167 (w), 822 (s), 739 (m), 616 (m), 555 (s) cm^{-1}. For ^1H and ^{13}C NMR spectra see ref. 3.

3,3'-(2-Butyne-1,4-diyl)bis(1-methylimidazolium) bis(bis(triflimide)) (1c). Yield: 82%, liquid. ^1H NMR (DMSO-*d*$_6$): δ 3.88 (s, 3H), 5.30 (s, 2H), 7.75 (s, 1H), 7.81 (s, 1H), 9.21 (s, 1H); ^{13}C NMR

(DMSO-d_6): δ 36.0, 38.6, 79.7, 119.5 (q, $J = 322$ Hz), 122.2, 124.1, 136.7; IR (neat): ν 3159 (w), 3125 (w), 1578 (w), 1345 (m), 1328 (m), 1173 (s), 1131 (s), 1050 (s), 789 (w), 739 (m), 609 (s), 568 (s), 508 (s) cm^{-1}.

3,3'-(2-Butyne-1,4-diyl)bis(1-methylimidazolium) bis(tetraphenylborate) (1d). Solutions of the chloride **1a** (80 mg, 0.3 mmol) in MeOH (3 mL) and ammonium tetraphenylborate (200 mg, 0.6 mmol) in MeOH (3 mL) were combined and stirred for 90 min. The precipitate was filtered off, washed with MeOH and dried to yield 98 mg (81%), mp 192–199 °C (decomposition). ^{1}H NMR (DMSO-d_6): δ 3.74 (s, 3H), 5.18 (s, 2H), 6.84 (t, $J = 7.5$ Hz, 4H), 6.98 (t, $J = 7.5$ Hz, 8H), 7.26 (s, 8H), 7.60 (s, 1H), 7.70 (s, 1H), 8.97 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 35.9, 38.5, 79.7, 121.6, 122.1, 124.0, 125.3, 135.6, 136.5, 163.4 (q, $J = 49$ Hz); IR (neat): ν 3159 (w), 3122 (w), 3054 (w), 2983 (w), 1572 (w), 1343 (w), 1171 (w), 1136 (w), 812 (w), 737 (s), 707 (s), 610 (m) cm^{-1}. Single-crystal diffraction: $T = 173(2)$ K; $\theta_{\max} = 25.4°$; indices $-10 \le h \le 11$, $-17 \le k \le 21$, $-16 \le l \le 12$; $D_x = 1.21$ g cm^{-3}; 14162 reflections measured, 4262 independent with $R_{\text{int}} = 0.042$, $F(000) = 908$, $\mu = 0.07$ mm^{-1}. Crystal data for **1d**, $C_{60}H_{56}B_2N_4$ ($M = 854.71$ g mol^{-1}): monoclinic, $P2_1/n$, $a = 9.9496(4)$, $b = 17.4877(9)$, $c = 13.5217(7)$ Å, $\beta = 96.420(4)°$, $V = 2338.0(2)$ Å^3, $Z = 2$. $R_1 = 0.047$ and $wR_2 = 0.099$ for 3092 reflections with $I > 2\sigma(I)$, $R_1 = 0.076$ and $wR_2 = 0.11$ for all data; $S = 1.02$; $\Delta\rho_{\max} = 0.19$ and $\Delta\rho_{\min} = -0.21$ e Å^{-3}. CCDC reference number 1504029.

3,3'-(2-Butyne-1,4-diyl)bis(1-methylimidazolium) dicobalt hexacarbonyl bis(hexafluoridophosphate) (2a). Yield: 0.24 g (82%), mp 150 °C (decomposition). ^{1}H NMR (acetonitrile-d_3): δ 3.90 (s, 3H), 5.54 (s, 2H), 7.48 (s, 1H), 7.58 (s, 1H), 8.66 (s, 1H); ^{13}C NMR (acetonitrile-d_3): δ 36.8, 52.3, 91.6, 123.7, 125.0, 136.8, 198.2 (3C); IR (neat): ν 3168 (w), 2108 (w), 2069 (m), 2042 (s), 1561 (w), 1433 (w), 1168 (w), 1031 (w), 952 (w), 844 (s), 826 (s), 741 (w), 656 (w), 625 (w), 557 (s), 529 (s), 509 (s), 445 (w) cm^{-1}. Single-crystal diffraction: $T = 173(2)$ K; $\theta_{\max} = 25.4°$; indices $-17 \le h \le 12$, $-20 \le k \le 20$, $-23 \le l \le 26$; $D_x = 1.89$ g cm^{-3}; 29845 reflections measured, 10175 independent with $R_{\text{int}} = 0.036$, $F(000) = 3136$, $\mu = 1.43$ mm^{-1}. Crystal data for **2a**, $C_{18}H_{16}Co_2N_4O_6P_2F_{12}$ ($M = 792.15$ g mol^{-1}): orthorhombic, $P2_12_12_1$, $a = 14.6534(2)$, $b = 17.4208(3)$, $c = 21.7956(4)$ Å, $V = 5563.9(2)$ Å^3, $Z = 8$. $R_1 = 0.041$ and $wR_2 = 0.105$ for 9514 reflections with $I > 2\sigma(I)$, $R_1 = 0.045$ and $wR_2 = 0.108$ for all data; $S = 1.09$; $\Delta\rho_{\max} = 0.95$ and $\Delta\rho_{\min} = -0.40$ e Å^{-3}. CCDC reference number 1504030.

3,3'-(2-Butyne-1,4-diyl)bis(1-methylimidazolium) dicobalt hexacarbonyl bis(bis(triflimide)) (2b). Yield: 89%, mp 104 °C. ^{1}H NMR (acetonitrile-d_3): δ 3.90 (s, 3H), 5.53 (s, 2H), 7.48 (s, 1H), 7.58 (s, 1H), 8.65 (s, 1H); ^{13}C NMR (acetonitrile-d_3): δ 36.7, 52.2, 91.6, 120.5 (q, $J = 320$ Hz), 123.5, 124.9, 136.6, 197.9 (3C); IR (neat): ν 2108 (w), 2052 (m), 2026 (m), 2011 (m), 1345 (m), 1320 (m), 1181 (s), 1133 (s), 1058 (m), 789 (w), 651 (w), 598 (s), 570 (m), 505 (s) cm^{-1}. Single-crystal diffraction: $T = 233(2)$ K; $\theta_{\max} = 26.0°$; indices $0 \le h \le 18$, $-13 \le k \le 13$, $-30 \le l \le 29$; $D_x = 1.86$ g cm^{-3}; 21796 reflections measured, 7407 independent with $R_{\text{int}} = 0.029$, $F(000) = 2112$, $\mu = 1.22$ mm^{-1}. Crystal data for **2b**, $C_{22}H_{16}Co_2N_6O_{14}S_4F_{12}$ (M

= 1062.51 g mol^{-1}): monoclinic, $P2_1/n$, a = 14.6760(2), b = 10.9862(1), c = 24.3332(4) Å, β = 104.598(1)°, V = 3796.7(1) Å^3, Z = 4. R_1 = 0.038 and wR_2 = 0.089 for 6434 reflections with $I > 2\sigma(I)$, R_1 = 0.045 and wR_2 = 0.092 for all data; S = 1.03; $\Delta\rho_{\mathrm{max}}$ = 0.50 and $\Delta\rho_{\mathrm{min}}$ = –0.46 e Å^{-3}. CCDC reference number 1504031.

3,3'-(2-Butyne-1,4-diyl)bis(1,2-dimethylimidazolium) dichloride (3a). Yield: 74%, mp 211 °C. ^{1}H NMR (DMSO-d_6): δ 2.65 (s, 3H), 3.80 (s, 3H), 5.35 (s, 2H), 7.73 (d, J = 2.0 Hz, 1H), 7.82 (d, J = 2.0 Hz, 1H); ^{13}C NMR (DMSO-d_6): δ 9.5, 34.9, 37.5, 79.2, 120.8, 122.6, 144.9; IR (neat): ν 3103 (w), 3061 (m), 3011 (m), 2885 (m), 1584 (m), 1532 (m), 1398 (m), 1354 (m), 1248 (m), 1191 (m), 1176 (m), 1119 (m), 793 (s), 768 (s), 720 (m) cm^{-1}.

3,3'-(2-Butyne-1,4-diyl)bis(1,2-dimethylimidazolium) bis(hexafluoridophosphate) (3b). Yield: 60%, mp 230 °C. ^{1}H NMR (DMSO-d_6): δ 2.61 (s, 3H), 3.77 (s, 3H), 5.24 (s, 2H), 7.66 (s, 1H), 7.69 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 9.3, 34.8, 37.4, 79.1, 120.7, 122.6, 144.8; IR (neat): ν 3160 (w), 1349 (w), 1247 (w), 828 (s), 742 (m), 674 (m), 556 (s) cm^{-1}.

3,3'-(2-Butyne-1,4-diyl)bis(1,2-dimethylimidazolium) bis(bis(triflimide)) (3c). Yield: 80%, mp 113 °C. ^{1}H NMR (DMSO-d_6): δ 2.61 (s, 3H), 3.77 (s, 3H), 5.24 (s, 2H), 7.66 (d, J = 2.0 Hz, 1H), 7.69 (d, J = 2.0 Hz, 1H); ^{13}C NMR (DMSO-d_6): δ 9.4, 34.9, 37.5, 79.1, 119.5 (q, J = 322 Hz), 120.8, 122.6, 144.9; IR (neat): ν 3154 (w), 1347 (m), 1333 (m), 1180 (s), 1137 (m), 1050 (s), 741 (m), 613 (s), 568 (m), 512 (m) cm^{-1}.

3,3'-(2-Butyne-1,4-diyl)bis(1,2-dimethylimidazolium) dicobalt hexacarbonyl bis(hexafluoridophosphate) (4a). Yield: 0.10 g (34%), mp 206 °C. ^{1}H NMR (acetonitrile-d_3): δ 2.61 (s, 3H), 3.75 (s, 3H), 5.47 (s, 2H), 7.38 (s, 1H), 7.44 (s, 1H); ^{13}C NMR (acetonitrile-d_3): δ 10.4, 36.1, 51.1, 90.9, 122.5, 124.1, 145.4, 198.6 (3C); IR (neat): ν 3162 (w), 2110 (w), 2074 (m), 2045 (s), 2026 (m), 1591 (w), 1536 (w), 1423 (w), 1391 (w), 1343 (w), 1272 (w), 1242 (w), 1166 (w), 945 (w), 824 (s), 767 (m), 742 (m), 724 (w), 667 (w), 620 (w), 556 (s), 525 (m), 508 (s), 446 (w), 412 (w) cm^{-1}. Single-crystal diffraction: T = 120(2) K; θ_{max} = 25.2°; indices $-16 \leq h \leq 16$, $-13 \leq k \leq 13$, $-23 \leq l \leq 22$; D_{x} = 1.82 g cm^{-3}; 24481 reflections measured, 2702 independent with R_{int} = 0.075, $F(000)$ = 1632, μ = 1.33 mm^{-1}. Crystal data for **4a**, $C_{20}H_{20}Co_2N_4O_6P_2F_{12}$ (M = 820.20 g mol^{-1}): orthorhombic, $Pbcn$, a = 14.1032(5), b = 11.0446(4), c = 19.2332(7) Å, V = 2995.8(2) Å^3, Z = 4. R_1 = 0.040 and wR_2 = 0.063 for 1993 reflections with $I > 2\sigma(I)$, R_1 = 0.071 and wR_2 = 0.069 for all data; S = 1.05; $\Delta\rho_{\mathrm{max}}$ = 0.43 and $\Delta\rho_{\mathrm{min}}$ = –0.38 e Å^{-3}. CCDC reference number 1504032.

3,3'-(2-Butyne-1,4-diyl)bis(1,2-dimethylimidazolium) dicobalt hexacarbonyl bis(bis(triflimide)) (4b). Yield: 0.31 g (72%), mp 108 °C. ^{1}H NMR (acetonitrile-d_3): δ 2.63 (s, 3H), 3.77 (s, 3H), 5.48 (s, 2H), 7.41 (s, 1H), 7.45 (s, 1H); ^{13}C NMR (acetonitrile-d_3): δ 10.4, 36.1, 51.1, 90.9, 120.8 (q, J = 320 Hz), 122.4, 124.1, 145.4, 198.6 (3C); IR (neat): ν 3149 (w), 2108 (m), 2066 (s), 2054 (s), 2036 (s), 2008 (s), 1591 (w), 1573 (w), 1535 (w), 1448 (w), 1418 (w), 1343 (s), 1328 (s), 1267 (w), 1232 (m), 1180 (s), 1133 (s), 1058 (s), 838 (w), 790 (m), 753 (m), 741 (m), 726 (w), 685 (w), 651 (m), 598 (s), 570 (s), 542 (m), 527 (m), 504 (s), 435 (w), 406 (w) cm^{-1}.

1,1'-(2-Butyne-1,4-diyl)bis(4-methyl-1,2,4-triazolium) dichloride (5a). Yield: 58%, mp 221 °C. ^{1}H NMR (DMSO-*d*$_6$): δ 3.94 (s, 3H), 5.63 (s, 2H), 9.26 (s, 1H), 10.61 (s, 1H); ^{13}C NMR (DMSO-*d*$_6$): δ 34.3, 41.6, 79.1, 143.6, 146.0; IR (neat): ν 3066 (w), 3000 (w), 2904 (m), 2796 (w), 1574 (m), 1524 (w), 1422 (w), 1352 (m), 1206 (w), 1167 (m), 1148 (m), 1086 (w), 1057 (m), 1000 (s), 959 (w), 931 (w), 898 (w), 772 (s), 653 (m), 640 (m), 622 (s) cm^{-1}.

1,1'-(2-Butyne-1,4-diyl)bis(4-methyl-1,2,4-triazolium) bis(hexafluoridophosphate) (5b). Yield: 78%, mp 162 °C. ^{1}H NMR (DMSO-*d*$_6$): δ 3.91 (s, 1H), 5.56 (s, 2H), 9.18 (s, 1H), 10.12 (s, 1H); ^{13}C NMR (DMSO-*d*$_6$): δ 34.3, 41.5, 78.8, 143.5, 146.0; IR (neat): ν 3161 (w), 1587 (w), 1361 (w), 1159 (w), 824 (s), 769 (m), 655 (w), 619 (m), 555 (s) cm^{-1}.

1,1'-(2-Butyne-1,4-diyl)bis(4-methyl-1,2,4-triazolium) bis(bis(triflimide) (5c). Yield: 77%, liquid. ^{1}H NMR (DMSO-*d*$_6$): δ 3.91 (s, 3H), 5.56 (s, 2H), 9.18 (s, 1H), 10.10 (s, 1H); ^{13}C NMR (DMSO-*d*$_6$): δ 34.3, 41.5, 78.8, 119.5 (q, $J = 322$ Hz), 143.5, 146.0; IR (neat): ν 3145 (w), 1586 (m), 1345 (m), 1174 (s), 1129 (s), 1049 (s), 887 (w), 790 (m), 764 (m), 741 (m), 611 (s), 599 (s), 569 (s), 509 (s) cm^{-1}.

1,1'-(2-Butyne-1,4-diyl)bis(4-methyl-1,2,4-triazolium) dicobalt hexacarbonyl bis(bis(triflimide) (6). Yield: 0.30 g (62%), mp 67 °C. ^{1}H NMR (acetonitrile-*d*$_3$): δ 3.95 (s, 3H), 5.76 (s, 2H), 8.69 (s, 1H), 9.48 (s, 1H); ^{13}C NMR (acetonitrile-*d*$_3$): δ 35.1, 55.0, 88.5, 120.5 (q, $J = 323$ Hz), 143.3, 146.4, 198.4 (3C); IR (neat): ν 3321 (s), 2945 (m), 2832 (m), 2106 (w), 2070 (m), 2043 (m), 1449 (m), 1353 (w), 1195 (s), 1137 (m), 1021 (s), 618 (s), 571 (s), 511 (s) cm^{-1}. Single-crystal diffraction: $T = 173(2)$ K; $\theta_{\max} = 25.4°$; indices $-18 \le h \le 16$, $-13 \le k \le 12$, $-26 \le l \le 27$; $D_x = 1.93$ g cm^{-3}; 22258 reflections measured, 6696 independent with $R_{\text{int}} = 0.039$, $F(000) = 2112$, $\mu = 1.27$ mm^{-1}. Crystal data for **6**, $C_{20}H_{14}Co_2F_{12}N_8O_{14}S_4$ ($M = 1064.49$ g mol^{-1}): monoclinic, $P2_1/n$, $a = 15.5641(4)$, $b = 10.9787(2)$, $c = 22.5588(6)$ Å, $\beta = 107.704(3)°$, $V = 3672.2(2)$ Å^3, $Z = 4$. $R_1 = 0.029$ and $wR_2 = 0.067$ for 5764 reflections with $I > 2\sigma(I)$, $R_1 = 0.037$ and $wR_2 = 0.071$ for all data; $S = 1.03$; $\Delta\rho_{\max} = 0.34$ and $\Delta\rho_{\min} = -0.32$ e Å^{-3}. CCDC reference number 1504033.

3,3'-(2-Butyne-1,4-diyl)bis(1-vinylimidazolium) dichloride (7a). Yield: 65%, mp >240 °C (decomposition). ^{1}H NMR (DMSO-*d*$_6$): δ 5.43 (s, 2H), 5.45 (dd, $J = 2.4$, 8.7 Hz, 1H), 6.07 (dd, $J = 2.4$, 15.7 Hz, 1H), 7.47 (dd, $J = 8.7$, 15.6 Hz, 1H), 8.09 (s, 1H), 8.32 (s, 1H), 10.11 (s, 1H); ^{13}C NMR (DMSO-*d*$_6$): δ 39.1, 80.0, 109.0, 119.2, 123.2, 128.8, 135.9; IR (neat): ν 3034 (m), 2926 (w), 1651 (m), 1580 (w), 1547 (s), 1368 (m), 1173 (s), 974 (m), 836 (m), 594 (s) cm^{-1}.

3,3'-(2-Butyne-1,4-diyl)bis(1-vinylimidazolium) bis(bis(triflimide)) (7b). Yield: 90%, mp 43 °C. For ^{1}H NMR spectra see ref. 18. ^{13}C NMR (DMSO-*d*$_6$): δ 39.1, 79.7, 109.3, 119.4, 119.5 (q, $J = 322$ Hz), 123.2, 128.8, 135.7; IR (neat): ν 3151 (w), 1555 (w), 1345 (m), 1175 (s), 1131 (s), 1050 (s), 952 (w), 739 (m), 610 (s), 598 (s), 568 (s), 508 (s) cm^{-1}. Single-crystal diffraction: $T = 173(2)$ K; $\theta_{\max} = 25.3°$; indices $-17 \le h \le 17$, $-16 \le k \le 16$, $-13 \le l \le 19$; $D_x = 1.77$ g cm^{-3}; 19264 reflections measured, 5482 independent with $R_{\text{int}} = 0.024$, $F(000) = 1608$, $\mu = 0.45$ mm^{-1}. Crystal data for **7b**, $C_{18}H_{16}F_{12}N_6O_8S_4$ ($M = 800.61$ g mol^{-1}): monoclinic, $P2_1/n$, $a = 14.3650(5)$, $b = 13.6793(4)$, $c = 16.5155(6)$ Å, $\beta = 112.354(4)°$, $V = 3001.5(2)$ Å^3, $Z = 4$. $R_1 = 0.032$ and $wR_2 = 0.080$ for 4745 reflections with $I > 2\sigma(I)$, $R_1 = 0.039$ and $wR_2 = 0.085$ for all data; $S = 1.04$; $\Delta\rho_{\max} = 0.33$ and $\Delta\rho_{\min} = -0.36$ e Å^{-3}. CCDC reference number 1504034.

3,3'-(2-Butyne-1,4-diyl)bis(1-vinylimidazolium) dicobalt hexacarbonyl bis(bis(triflimide)) (8). Yield: 92%, mp 92 °C. ^{1}H NMR (acetonitrile-d_3): δ 5.51 (d, $J = 8.7$ Hz, 1H), 5.62 (s, 2H), 5.88 (d, $J = 15.6$ Hz, 1H), 7.22 (dd, $J = 15.6$, 8.7 Hz, 1H), 7.72 (s, 1H), 7.86 (s, 1H), 8.98 (s, 1H); ^{13}C NMR (acetonitrile-d_3): δ 52.5, 90.9, 110.6, 120.1 (q, $J = 321$ Hz), 120.5, 124.2, 128.5, 134.9, 197.8 (3C); IR (neat): ν 3144 (w), 2109 (m), 2057 (m), 2028 (m), 2011 (m), 1554 (w), 1319 (m), 1190 (s), 1136 (s), 1060 (m), 655 (m), 598 (m), 506 (s) cm^{-1}. Single-crystal diffraction: $T = 193(2)$ K; $\theta_{\max} = 25.5°$; indices $-13 \le h \le 13$, $-15 \le k \le 15$, $-18 \le l \le 18$; $D_x = 1.85$ g cm^{-3}; 64405 reflections measured, 7276 independent with $R_{\text{int}} = 0.031$, $F(000) = 1080$, $\mu = 1.19$ mm^{-1}. Crystal data for **8**, $C_{24}H_{16}Co_2F_{12}N_6O_{14}S_4$ ($M = 1086.53$ g mol^{-1}): triclinic, $P\bar{1}$, $a = 10.9950(4)$, $b = 12.6973(5)$, $c = 14.9727(6)$ Å, $\alpha = 71.258(1)°$, $\beta = 82.750(1)°$, $\gamma = 82.634(1)°$, $V = 1955.1(2)$ Å^3, $Z = 2$. $R_1 = 0.030$ and $wR_2 = 0.074$ for 6569 reflections with $I > 2\sigma(I)$, $R_1 = 0.034$ and $wR_2 = 0.077$ for all data; $S = 1.05$; $\Delta\rho_{\max} = 0.78$ and $\Delta\rho_{\min} = -0.59$ e Å^{-3}. CCDC reference number 1504035.

ACKNOWLEDGEMENTS

We are grateful to H. Kopacka for the NMR spectra.

REFERENCES

1. M. Yang, K. Stappert, and A.-V. Mudring, *J. Mater. Chem. C*, 2014, **2**, 458.
2. J. E. Bara, E. S. Hatakeyama, B. R. Wiesenauer, X. Zeng, R. D. Noble, and D. L. Gin, *Liq. Cryst.*, 2010, **37**, 1587.
3. A. Liu, X. Zhang, W. Chen, and H. Qiu, *Inorg. Chem. Commun.*, 2008, **11**, 1128.
4. J. L. Anderson and D. W. Armstrong, *Anal. Chem.*, 2005, **77**, 6453.
5. M. H. Rao and K. Muralidharan, *Dalton Trans.*, 2013, **42**, 8854.
6. Z. Fei, D. Zhao, R. Scopelliti, and P. J. Dyson, *Organometallics*, 2004, **23**, 1622.
7. H. Schottenberger, K. Wurst, U. E. I. Horvath, S. Cronje, J. Lukasser, J. Polin, J. M. McKenzie, and H. G. Raubenheimer, *Dalton Trans.*, 2003, 4275.
8. H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, R. Markby, and I. Wender, *J. Am. Chem. Soc.*, 1954, **76**, 1457.
9. H. Greenfield, H. W. Sternberg, R. A. Friedel, J. Wotiz, R. Markby, and I. Wender, *J. Am. Chem.*

Soc., 1956, **78**, 120.

10. C.-S. Guo, C.-M. Weng, and F.-E. Hong, *Eur. J. Inorg. Chem.*, 2010, 3220.
11. F. Baert, A. Guelzim, and P. Coppens, *Acta Cryst.*, 1984, **B40**, 590.
12. G. Laus, M. Hummel, D. M. Többens, T. Gelbrich, V. Kahlenberg, K. Wurst, U. J. Griesser, and H. Schottenberger, *CrystEngComm*, 2011, **13**, 5439.
13. G. Bentivoglio, A. Schwärzler, K. Wurst, V. Kahlenberg, G. Nauer, G. Bonn, H. Schottenberger, and G. Laus, *J. Chem. Crystallogr.*, 2009, **39**, 662.
14. M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, and R. Spagna, *J. Appl. Cryst.*, 2003, **36**, 1103.
15. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
16. L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849.
17. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466.
18. Y. C. Hudiono, A. L. Miller, P. W. Gibson, A. L. LaFrate, R. D. Noble, and D. L. Gin, *Ind. Eng. Chem. Res.*, 2012, **51**, 7453.