[n]STAFFANES WITH TERMINAL NITRILE AND ISONITRILE FUNCTIONALITIES AND THEIR METAL COMPLEXES

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Dedicated to Professor Václav Horák on the occasion of his 70th birthday.

The synthesis of several bridgehead nitrile and isonitrile derivatives of the first two [n]staffanes, n = 1 and 2, is reported. Both isonitriles were converted into pentacarbonylmolybdenum complexes. [2]Staffane-3-carbonitrile was converted to a complex with rhodium(II) acetate, which was characterized by a single crystal X-ray analysis.

Terminally substituted [n]staffanes[1-5] *I* offer promise as reasonably rigid molecular spacers and as rod-shaped construction elements in the assembly of molecular structures of the "Tinkertoy" type[1-3]. One of the uses of such spacers is in electron transfer studies, in which transition metal complexes frequently serve as donors and acceptors. Also, one of the possible modes of attachment of rod termini to connectors in molecular-scale fabrication involves the use of transition metal based "spools"[1]. For both reasons, we are interested in the preparation and properties of [n]staffanes carrying ligand functionalities at the bridgehead positions. The nitrile and isonitrile groups permit a strictly linear attachment to a metal center and therefore appear particularly suitable for our purposes. The preparation of these compounds thus is the first objective of the present paper.

A potential complication may be anticipated in that the bridgehead position in the bicyclo[1.1.1]pentane cage in [n]staffanes forms exocyclic bonds using an hybrid orbital of unusually high *s* character, imposed by the small endocyclic valence angles, and

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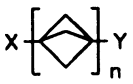
this may modify the ligand characteristics of the –CN and –NC groups by reducing their σ donation capability. Our second objective therefore is the preparation and structural characterization of model transition metal complexes of this type.

We now report the synthesis of several bridgehead nitriles and isonitriles derived from the first two [n]staffanes and the preparation of their transition metal complexes.

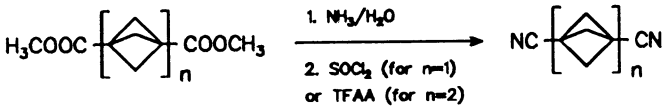


I

RESULTS AND DISCUSSION

The starting materials for the nitrile and isonitrile syntheses are the [n]staffane-3-carboxylic[2,3] and [n]staffane-3,3$^{(n-1)}$-dicarboxylic[3,5] acids, which are in turn accessible from [1.1.1]propellane[6]. Since even the higher members of the dicarboxylic acid series have now been synthesized, albeit in low yields[3], it can be anticipated that the procedures described here for the first two members will provide access to even longer dinitriles and diisonitriles of the staffane series.

Scheme 1 shows the transformation of the diamides, obtained from the diesters *II* and *III* or the monoester *I* (n = 2, X = H, Y = COOMe) and ammonia under slight pressure, to the dinitriles *IV* and *V* and the mononitrile *I* (n = 2, X = H, Y = CN). This was effected with thionyl chloride (for n = 1) or trifluoroacetic anhydride and pyridine[7] (for n = 2). Thionyl chloride did not give acceptable results for the nitriles derived from [2]staffane.



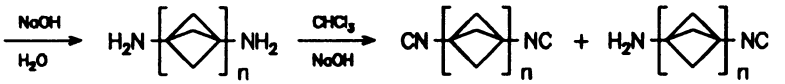
II, n = 1
III, n = 2

IV, n = 1
V, n = 2

SCHEME 1

The Curtius rearrangement path from the diacids *VI* and *VII* via the dichlorides *VIII* and *IX* and the hydrochlorides *X* and *XI* to the diamines *XII* and *XIII* and further to the diisonitriles *XIV* and *XV* by reaction with dichlorocarbene under phase transfer conditions[8] (Scheme 2) also yielded the aminoisonitriles *XVI* and *XVII* as easily separable by-products. Attempts to force the reaction to completion by extending the reaction time actually gave lower yields of the diisonitriles due to decomposition. The synthesis of the monofunctional [2]staffane-3-isonitrile (*I*, n = 2, X = H, Y = NC) was analogous.

VI, n = 1 *VIII*, n = 1 *X*, n = 1
VII, n = 2 *IX*, n = 2 *XI*, n = 2

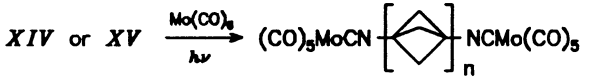


XII, n = 1 *XIV*, n = 1 *XVI*, n = 1
XIII, n = 2 *XV*, n = 2 *XVII*, n = 2

SCHEME 2

In order to test the suitability of the diisonitriles for the assembly of more complicated structures by attachment to transition metal centers, we have run a few model reactions. Since the bridgehead position of bicyclo[1.1.1]pentane is quite strongly electron withdrawing, as judged, e.g., by the gas phase acidity of the bridgehead hydrogen[9], one could suspect that the bridgehead isonitrile group will have less pronounced sigma donor properties than ordinary alkyl isonitriles.

Indeed, the latter undergo a thermal reaction with iron pentacarbonyl to completion in boiling benzene in 0.5 h (ref.[10]), yet *XIV* did not show any sign of reaction under these conditions after 4 h. A thermal reaction with tris(acetonitrile)tricarbonylmolybdenum proceeded fairly rapidly, but yielded an insoluble precipitate of presumed polymeric structure, even when *XIV* was present in large excess. However, the desired products *XVIII* and *XIX* were obtained readily by irradiation of molybdenum hexacarbonyl in the presence of the diisonitriles *XIV* and *XV*, respectively (Scheme 3). This method of producing mixed carbonyl–isonitrile complexes of molybdenum seems not to have been used before, but worked very well in our case.



XVIII, n = 1
XIX, n = 2

SCHEME 3

The bis([2]staffane-3-carbonitrile)dirhodium(II) tetraacetate complex is readily formed by treating dirhodium(II) tetraacetate with two equivalents of [2]staffane-3-carbonitrile in $CHCl_3$ at 40 °C.

The crystal structure of the complex is depicted in Fig. 1.

The molecule has the anticipated linear structure suitable for the use of Rh_2 as a spool in a construction set. It contains an inversion center located at the middle of the Rh–Rh bond. Hence, only the Rh–Rh bond length and half of the remaining bond lengths and bond angles shown in Fig. 1 are independent. They are listed in Tables I and II. The intercage bond length C(10)–C(11) in the complex is the longest (1.497 Å) among the intercage bonds observed in [n]staffanes so far (1.47 – 1.48 Å; ref.[11]). The Rh–N and N≡C bonds shown in Table III are 0.06 Å shorter and 0.02 Å longer, respectively, than those reported[12] in $Rh_2(O_2CCH_3)_4(NCCH_3)_2$. In our dirhodium(II) complex the non-bonded distances between bridgeheads are unexceptional (Table III). The distance is slightly longer in the nitrile substituted cage [C(6)–C(10), 1.863 Å] than in the unsubstituted cage [C(11)–C(15), 1.854 Å]. It is interesting to note that the

TABLE I
Bond lengths[a] (Å) for $C_{30}H_{38}N_2O_8Rh_2 \cdot 6\ CHCl_3$

Bond	Bond length	Bond	Bond length
Rh(1)–O(1)	2.032(4)	Rh(1)–O(2)	2.024(5)
Rh(1)–O(3)	2.038(4)	Rh(1)–O(4)	2.038(4)
Rh(1)–N(1)	2.202(7)	Rh(1)–Rh(1A)	2.384(1)
O(1)–C(1)	1.267(9)	O(2)–C(2)	1.253(9)
O(3)–C(1A)	1.266(9)	O(4)–C(2A)	1.266(9)
N(1)–C(5)	1.138(10)	C(1)–C(3)	1.500(10)
C(1)–O(3A)	1.266(9)	C(2)–C(4)	1.520(9)
C(2)–O(4A)	1.266(9)	C(5)–C(6)	1.447(11)
C(6)–C(7)	1.545(11)	C(6)–C(8)	1.548(10)
C(6)–C(9)	1.546(11)	C(7)–C(10)	1.546(11)
C(8)–C(10)	1.545(10)	C(9)–C(10)	1.543(11)
C(10)–C(11)	1.497(11)	C(11)–C(12)	1.554(12)
C(11)–C(13)	1.529(12)	C(11)–C(14)	1.545(11)
C(12)–C(15)	1.533(12)	C(13)–C(15)	1.532(13)
C(14)–C(15)	1.527(12)	C(16)–Cl(1)	1.721(8)
C(16)–Cl(2)	1.747(9)	C(16)–Cl(3)	1.730(9)
C(17)–Cl(4)	1.731(9)	C(17)–Cl(5)	1.751(9)
C(17)–Cl(6)	1.754(9)	C(18)–Cl(7)	1.750(8)
C(18)–Cl(8)	1.759(8)	C(18)–Cl(9)	1.741(8)

[a] Non-bonded distances: C(6)–C(10) 1.863(11), C(11)–C(15) 1.854(12).

Rh(1)–O(2) bond is significantly shorter than the other three Rh–O bonds. This seems attributable to the unsymmetrical hydrogen bonding among the solvent $CHCl_3$ molecules and the oxygen atoms of acetates (Fig. 2).

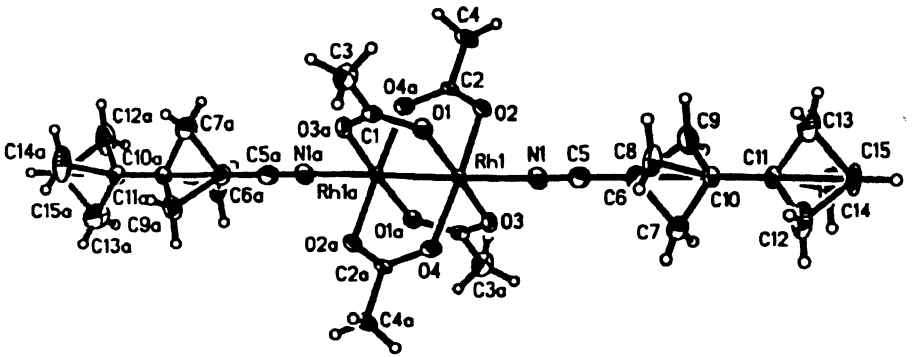


FIG. 1
The structure of the $Rh_2(O_2CCH_3)_4(NCC_{10}H_{13})_2$ molecule with an atom labeling scheme

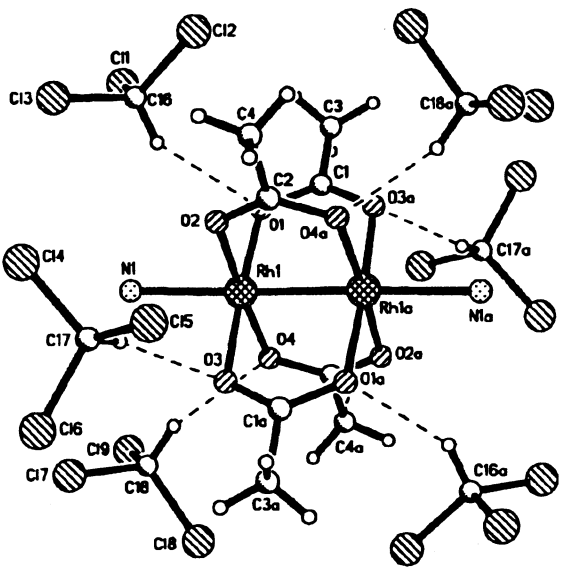
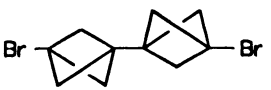
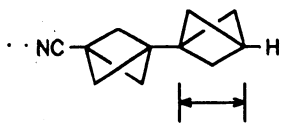
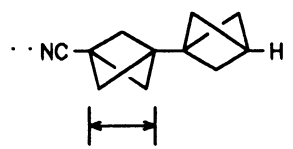


FIG. 2
A representation of the $Rh_2(O_2CCH_3)_4$ fragment of $Rh_2(O_2CCH_3)_4(NCC_{10}H_{13})_2 \cdot 6\ CHCl_3$, showing hydrogen bonding interaction between the chloroform hydrogen atoms and acetate oxygen atoms. The relevant distances are H(16)–O(1): 2.49 Å; H(17)–O(3): 2.26 Å; H(18)–O(4): 2.34 Å. The hydrogen atom closest to O(2) is 2.59 Å away

TABLE II
Bond angles (°) for $C_{30}H_{38}N_2O_8Rh_2$. 6 $CHCl_3$

Atoms	Bond angle	Atoms	Bond angle
O(1)–Rh(1)–O(2)	89.2(2)	O(1)–Rh(1)–O(3)	176.2(2)
O(2)–Rh(1)–O(3)	90.3(2)	O(1)–Rh(1)–O(4)	91.5(2)
O(2)–Rh(1)–O(4)	175.9(2)	O(3)–Rh(1)–O(4)	88.7(2)
O(1)–Rh(1)–N(1)	90.5(2)	O(2)–Rh(1)–N(1)	90.7(2)
O(3)–Rh(1)–N(1)	93.2(2)	O(4)–Rh(1)–N(1)	93.3(2)
O(1)–Rh(1)–Rh(1A)	88.6(1)	O(2)–Rh(1)–Rh(1A)	88.5(1)
O(3)–Rh(1)–Rh(1A)	87.7(1)	O(4)–Rh(1)–Rh(1A)	87.5(1)
N(1)–Rh(1)–Rh(1A)	178.8(2)	Rh(1)–O(1)–C(1)	118.8(4)
Rh(1)–O(2)–C(2)	119.1(4)	Rh(1)–O(3)–C(1A)	119.5(4)
Rh(1)–O(4)–C(2A)	119.1(4)	Rh(1)–N(1)–C(5)	178.5(6)
O(1)–C(1)–C(3)	116.3(6)	O(1)–C(1)–O(3A)	125.4(6)
C(3)–C(1)–O(3A)	118.3(6)	O(2)–C(2)–C(4)	118.3(6)
O(2)–C(2)–O(4A)	125.8(6)	C(4)–C(2)–O(4A)	115.9(6)
N(1)–C(5)–C(6)	178.2(8)	C(5)–C(6)–C(7)	126.9(6)
C(5)–C(6)–C(8)	128.0(6)	C(7)–C(6)–C(8)	87.2(6)
C(5)–C(6)–C(9)	126.4(7)	C(7)–C(6)–C(9)	88.0(6)
C(8)–C(6)–C(9)	86.9(6)	C(6)–C(7)–C(10)	74.1(5)
C(6)–C(8)–C(10)	74.1(5)	C(6)–C(9)–C(10)	74.2(5)
C(7)–C(10)–C(8)	87.2(6)	C(7)–C(10)–C(9)	88.1(6)
C(8)–C(10)–C(9)	87.2(6)	C(7)–C(10)–C(11)	126.1(6)
C(8)–C(10)–C(11)	128.9(6)	C(9)–C(10)–C(11)	126.0(6)
C(10)–C(11)–C(12)	127.3(6)	C(10)–C(11)–C(13)	128.5(7)
C(12)–C(11)–C(13)	86.7(6)	C(10)–C(11)–C(14)	126.4(6)
C(12)–C(11)–C(14)	86.2(6)	C(13)–C(11)–C(14)	87.9(6)
C(11)–C(12)–C(15)	73.8(6)	C(11)–C(13)–C(15)	74.6(6)
C(11)–C(14)–C(15)	74.3(6)	C(12)–C(15)–C(13)	87.3(7)
C(12)–C(15)–C(14)	87.5(7)	C(13)–C(15)–C(14)	88.5(7)
Cl(1)–C(16)–Cl(2)	109.7(5)	Cl(1)–C(16)–Cl(3)	111.0(5)
Cl(2)–C(16)–Cl(3)	112.0(5)	Cl(4)–C(17)–Cl(5)	111.5(5)
Cl(4)–C(17)–Cl(6)	110.5(5)	Cl(5)–C(17)–Cl(6)	108.6(4)
Cl(7)–C(18)–Cl(8)	109.5(4)	Cl(7)–C(18)–Cl(9)	110.8(4)
Cl(8)–C(18)–Cl(9)	111.1(4)		

TABLE III
A comparison of non-bonded distances between bridgeheads in [n]staffane derivatives

Compounds	Non-bonded distance	Reference
	1.845	13
	1.850	14
	1.874	11
	1.824	11
	1.854	this work
	1.863	this work

EXPERIMENTAL

Melting points were determined on a Boetius PHMKO5 apparatus with microscope attachment (4 °C/min). ^1H and ^{13}C NMR (δ, ppm; *J*, Hz) spectra were run on a Nicolet NT-360 instrument in $CDCl_3$ or hexadeuterio acetone. IR spectra (cm^{-1}) were taken on a Nicolet 60SXR FTIR instrument in $CHCl_3$ or KBr. Mass spectra were taken on a 5995 Hewlett–Packard instrument. Elemental analyses were performed by Atlantic Microlabs, Norcross, Georgia.

[1]Staffane-1,3-dicarbonitrile (*IV*)

Dimethyl bicyclo[1.1.1]pentane-1,3-dicarboxylate[5] (*II*, 0.55 g, 3 mmol) was dissolved in THF (10 ml) and aqueous ammonia (10 ml) was added. The mixture was stirred at 50 °C for several hours. When the conversion was complete the mixture was evaporated and dried in vacuum. The white residue was refluxed with thionyl chloride (10 ml) for 2 h and excess thionyl chloride was evaporated. The residue was purified on silica gel column using ethyl acetate as an eluent, followed by sublimation (75 °C/22 mm Hg), yielding 0.29 g of white crystals *IV* (82% overall yield), m.p. 147 °C; ^1H NMR spectrum: 2.69 (s). ^{13}C NMR spectrum: 26.65, 57.28, 115.60. IR spectrum: 1 457, 2 235 and 2 244 (CN). EI MS, *m/z* (rel. int., %): 117 (M – 1, 14), 91 (100), 64 (42). For $C_7H_6N_2$ (118.1) calculated: 71.16% C, 5.12% H, 23.72% N; found: 71.23% C, 5.14% H, 23.62% N.

3-Carbamido-[1]staffane-1-carboxylic Acid

A sample of this material prepared according to the reported procedure[5] (850 mg, 5 mmol) was further purified. It was dissolved in aqueous ammonia (10 ml) and stirred at 50 °C overnight. The solution was concentrated, carefully acidified with hydrochloric acid, and the chilled suspension was filtered off to give a white powder of the product (0.72 g). The product was recrystallized from water to give an analytical sample, m.p. > 275 °C (dec.). ^1H NMR spectrum (hexadeuterioacetone): 2.26 (s). IR spectrum (KBr): 1 207, 1 313, 1 426, 1 591, 1 655, 1 710, 2 595, 3 195, 3 354. EI MS, *m/z* (rel. int., %): 156 (3), 155 (3), 154 (3), 138 (13), 137 (12), 111 (23), 110 (100), 82 (64), 67 (74), 66 (46), 65 (58). For $C_7H_9NO_3$ (157.2) calculated: 54.18% C, 5.85% H, 9.03% N; found: 54.27% C, 5.91% H, 8.89% N.

[1]Staffane-1,3-dicarbonitrile-^{15}N (*IV*-^{15}N)

Crude 3-carbamido[1]staffane-1-carboxylic acid (0.50 g, 3.2 mmol) was refluxed with thionyl chloride (3 ml) for 4 h, the excess of reagent was evaporated and the residue was vacuum dried. The crude carbonyl chloride was dissolved in methylene chloride (6 ml) and slowly added to the cold and stirred solution prepared from ammonium-^{15}N sulfate* (0.35 g) and 5% NaOH (7 ml) (ref.[15]). The two-phase mixture was stirred for 5 h, methylene chloride was evaporated and the chilled suspension of the amide was filtered off. The crude amide was refluxed with thionyl chloride (3 ml) for 3 h and excess thionyl chloride was evaporated. The residue was purified on silica gel column using ethyl acetate as an eluent, followed by sublimation (at 75 °C/22 mmHg), and yielded 0.28 g of white crystals of *IV*-^{15}N (74% overall yield), m.p. 147 °C. ^1H NMR spectrum: 2.68 (s). ^{13}C NMR spectrum: 26.64, 57.27, 115.55 (t, J = 8.6), 115.58. IR spectrum: 1 457, 2 214, 2 220, 2 244 (CN). EI MS, *m/z* (rel. int., %): 118 (M – 1, 8.5), 92 (M – CN, 97), 91 (M – $C^{15}N$, 93), 64 (100), 52 (63).

* The 99% isotopically pure ammonium-^{15}N sulfate was purchased from MSD.

[2]Staffane-3,3'-dicarbonitrile (*V*)

A mixture of dimethyl [2]staffane-3,3'-dicarboxylate[3] (*III*, 0.55 g, 2.2 mmol), and 30% aqueous ammonia (10 ml) in dioxane (10 ml) was stirred at 80 °C in a pressure bottle for several hours. Progress of the reaction was monitored by ^{1}H NMR. When the conversion was complete, the mixture was evaporated and dried in vacuum. Dry dioxane (10 ml) and pyridine (0.70 g, 8.8 mmol) were then added to the white residue and the resultant mixture was cooled to 3 °C. Trifluoroacetic anhydride (1.01 g, 4.8 mmol) was added dropwise to the stirred mixture at such a rate that the temperature was kept below 5 °C. The reaction was then allowed to warm to room temperature and stirring was continued for another 4 h. The pyridinium salt was removed by filtration and the filtrate was diluted with chloroform (10 ml), washed with water (2 × 5 ml), dried and evaporated. Finally, the crude product was purified on silica gel column using ethyl acetate–hexane (8 : 2) mixture as an eluent, followed by sublimation (95 °C/18 mm Hg) to give white crystals of *V* (0.22 g, 54%), m.p. 214 °C. ^{1}H NMR spectrum: 2.07 (s). ^{13}C NMR spectrum: 23.09, 42.55, 53.26, 117.25. IR spectrum: 2 229 (CN). MS, *m/z* (rel. int., %): 184 (M, 1.7), 116 (53), 91 (100), 65 (41). For $C_{12}H_{12}N_2$ (184.3) calculated: 78.22% C, 6.57% H, 15.21% N; found: 78.16% C, 6.56% H, 15.26% N.

[2]Staffane-3-carbonitrile (*I*, n = 2, X = H, Y = CN)

Crude [2]staffane-3-carbonyl chloride, prepared from [2]staffane-3-carboxylic acid[3] (0.5 g), was refluxed for 15 min in methanol (10 ml). The reaction mixture was evaporated, the resulting crude methyl [2]staffane-3-carboxylate (*I*, n = 2, X = H, Y = COOMe) was dissolved in THF (10 ml), and aqueous ammonia (10 ml) was added. The mixture was stirred at 50 °C for several hours. When the ester was no longer detectable by GC, the mixture was evaporated and dried in vacuum. The white residue was refluxed with thionyl chloride (10 ml) for 2 h. Excess thionyl chloride was evaporated and the residue was passed through a silica gel column and then sublimed (55 °C/20 mm Hg) to give [2]staffane-3-carbonitrile (*I*, n = 2, X = H, Y = CN, 50% overall yield), m.p. 129.5 °C. ^{1}H NMR spectrum: 1.64 (s, 6 H); 2.05 (s, 6 H); 2.40 (s, 1 H). ^{13}C NMR spectrum: 22.75, 26.65, 43.74, 44.08, 49.21, 53.20, 118.09. IR spectrum: 1 118, 1 448, 2 230 (CN), 2 876. EI MS, *m/z* (rel. int., %): 158 (M – 1, 3), 117 (41), 116 (40), 93 (36), 91 (100), 77 (81). For $C_{11}H_{13}N$ (159.2) calculated: 82.97% C, 8.23% H, 8.80% N; found: 82.94%C, 8.25% H, 8.87% N.

[2]Staffane-3,3'-dicarbonyl Dichloride (*IX*)

The diacid *VII* (ref.[3]) (1.5 g, 6.75 mmol) and thionyl chloride (3.0 ml) were refluxed until a clear solution was formed (about 12 h). Excess thionyl chloride was evaporated, and the crystalline residue was sublimed (95 °C/2 mm Hg) to give dichloride *IX* (1.60 g, 91%), m.p. 136 – 137 °C. ^{1}H NMR spectrum: 2.04 (s). ^{13}C NMR spectrum: 38.20, 44.70, 51.77, 170.78. IR spectrum: 1 786 (C=O). MS, *m/z* (rel. int., %): 225 (M – Cl, 0.3), 223 (M – Cl, 0.7), 131 (90), 91 (100), 65 (60). For $C_{12}H_{12}Cl_2O_2$ (259.2) calculated: 55.62% C, 4.67% H, 27.36% Cl; found: 55.71 C, 4.70% H, 27.31% Cl.

[1]Staffane-1,3-diamine (*XII*)

A mixture of the dichloride *VIII* (ref.[5]) (0.96 g, 5 mmol), sodium azide (0.97 g, 15 mmol) and benzyltriethylammonium chloride (57 mg, 0.25 mmol) in benzene (50 ml) was refluxed for 1 – 2 h. Progress of the reaction was followed by GC. After the reaction was completed the mixture was cooled and filtered. Concentrated hydrochloric acid (15 ml) was added to the filtrate, and the reaction mixture was stirred for 10 h at room temperature. The aqueous layer was separated. The benzene layer was washed with water (10 ml), and the combined aqueous layers were concentrated in high vacuum. The residue was washed with ether (2 × 10 ml) to give the ammonium salt *X*. Then 10% aqueous sodium hydroxide solution (5 ml) was added to *X*, the resulting solution was saturated with sodium chloride, extracted with methylene chloride (4 × 10 ml), and dried. Evaporation of the solvent and sublimation of the crude product

(40 °C/40 mm Hg) gave the diamine *XII* (0.38 g, 77%), m.p. 66 °C. ^{1}H NMR spectrum: 1.74 (bs, 4 H); 1.85 (s, 6 H). ^{13}C NMR spectrum: 45.52, 56.23. IR spectrum: 3 340, 3 253 (NH). MS, *m/z* (rel. int., %): 98 (M, 18), 97 (32), 57 (43), 42 (100).

[1]Staffane-1,3-diamine dihydrochloride (X). For $C_5H_{10}N_2$. 2 HCl (171.1) calculated: 35.10% C, 7.07% H, 41.45% Cl, 16.36% N; found: 35.01% C, 7.04% H, 41.36% Cl, 16.30% N.

[2]Staffane-3,3'-diamine (*XIII*)

The diamine *XIII* was prepared from the dichloride *IX* (1.30 g, 5.0 mmol) by the procedure described above for *XII*. The only difference was that the reaction mixture was heated to 50 °C to avoid the facile polymerization of the intermediate diisocyanate. Sublimation of the crude product (70 °C/15 mm Hg) gave white crystals of *XIII* (0.59 g, 72%), m.p. 111 °C. ^{1}H NMR spectrum: 1.56 (s, 12 H); 1.65 (bs, 4 H). ^{13}C NMR spectrum: 33.06, 48.20, 52.66. IR spectrum: 3 385, 3 324 (NH). MS, *m/z* (rel. int., %): 164 (M, 2.2), 122 (84), 108 (87), 107 (74), 106 (100), 91 (40), 42 (97). For $C_{10}H_{16}N_2$ (164.3) calculated: 73.12% C, 9.82% H, 17.06% N; found: 73.03% C, 9.78% H, 17.11% N.

[1]Staffane-1,3-diisonitrile *XIV* and 1-Amino-[1]staffane-3-isonitrile *XVI*

To a stirred solution of the diamine *XII* (0.39 g, 4.0 mmol), chloroform (1.19 g, 10.0 mmol) and benzyltriethylammonium chloride (90 mg, 0.4 mmol) in dichloromethane (4 ml), 50 % aqueous sodium hydroxide solution (3 ml) was added in one portion. Almost instantly a slightly exothermic reaction started, and the mixture was stirred at room temperature for 2 h. Water (10 ml) was added and products were extracted with dichloromethane (3 × 15 ml). The dichloromethane phase was washed with water and dried. Evaporation of the solvent gave a dark residue which was extracted with ether (3 × 10 ml). Evaporation of the ether provided a mixture of the crude products *XIV* and *XVI*. Separation and purification was accomplished by column chromatography on silica gel. Elution with chloroform yielded pure *XIV* (0.19 g, 40%) followed by *XVI*. The latter was further purified by sublimation (50 °C/20 mm Hg) to give white crystals (0.09 g, 21%). The diisonitrile *XIV* decomposes slowly at room temperature when left neat, but can be stored for at least a week in a refrigerated solution. Longer reaction time (3 – 4 h) made conversion of the reaction more complete but at the same time gave a lower yield of *XIV*. Diisonitrile *XIV*, m.p. > 80 °C (dec.). ^{1}H NMR spectrum: 2.66 (s). ^{13}C NMR spectrum: 53.35, 59.49, 161.39. IR spectrum: 2 134 (NC). MS, *m/z* (rel. int., %): 118 (M, 1.6), 91 (20, 92 (40), 64 (99), 52 (83), 39 (100). HR MS, *m/z*: 118.0761; (calculated for $C_7H_6N_2$ 118.0782). Isonitrile *XVI*, m.p. 69 °C. ^{1}H NMR spectrum: 1.73 (bs, 2 H); 2.24 (s, 6 H). ^{13}C NMR spectrum: 38.46 (t, J = 7), 48.01 (t, J = 6), 57.82, 157.59 (t, J = 7). IR spectrum: 3 345, 3 274 (NH), 2 124 (NC). MS, *m/z* (rel. int., %): 108 (M, 14), 107 (39), 81 (71), 41 (100), 39 (57). For $C_6H_8N_2$ (108.1) calculated: 66.64% C, 7.45% H, 25.91% N; found: 66.49% C, 7.43% H, 25.79% N.

[2]Staffane-3,3'-diisonitrile (*XV*) and 3-Amino[2]staffane-3'-isonitrile (*XVII*)

The isonitriles *XV* and *XVII* were prepared from the corresponding diamine *XIII* (0.40 g, 2.46 mmol) by the procedure described above. The reaction started after 10 – 15 min of induction period and the mixture was stirred for 3 h. Column chromatography of the crude products (silica gel, elution with chloroform) gave the pure diisonitrile *XV* (0.19 g, 42%) followed by *XVII*. The latter was further purified by sublimation (60 °C/10 mm Hg) to give white crystals (0.05 g, 12%). Diisonitrile *XV*, m.p. > 130 °C (dec.). ^{1}H NMR spectrum: 2.05 (s). ^{13}C NMR spectrum: 35.66, 40.44 (t, J = 6), 54.54, 156.48. IR spectrum: 2 136, 2 117 (NC). MS, *m/z* (rel. int., %): 184 (M, 0.5), 115 (70), 91 (100), 65 (45). For $C_{12}H_{12}N_2$ (184.3) calculated: 78.22% C, 6.57% H, 15.21% N; found: 78.17% C, 6.60% H, 15.11% N. Isonitrile *XVII*, m.p. 106 °C. ^{1}H NMR spectrum: 1.61 (s, 2 H); 1.64 (s, 2 H); 2.00 (s, 6 H). ^{13}C NMR spectrum: 32.33, 36.65 (t, J = 5), 40.56 (t, J = 5), 48.43, 52.75, 54.43, 155.15 (t, J = 5). IR spectrum: 3 387, 3 323 (NH), 2 135, 2 121 (NC).

MS, *m/z* (rel. int., %): 174 (M, 9), 173 (19), 146 (99), 132 (100), 106 (84), 91 (83). For $C_{11}H_{14}N_2$ (174.2) calculated: 75.82% C, 8.10% H, 16.08% N; found: 75.73% C, 8.14% H, 16.04% N.

[2]Staffane-3-isonitrile (*I*, n = 2, X = H, Y = NC)

[2]Staffane-3-carboxylic acid[3] (0.25 g, 1.4 mmol) and thionyl chloride (1 ml) were refluxed for 3 h. Excess thionyl chloride was evaporated to give the corresponding acid chloride. A mixture of crude acid chloride, sodium azide (0.14 g, 2.1 mmol) and benzyltriethylammonium chloride (10 mg, 0.4 mmol) in benzene (10 ml) was refluxed for 2 h, cooled and filtered. Concentrated hydrochloric acid (3 ml) was added to the filtrate and the reaction mixture was stirred for 5 h at room temperature. The aqueous layer was separated, the benzene layer washed with water (3 ml), and the combined aqueous layers were concentrated in high vacuum. The residue was washed with ether (2 × 5 ml) to give 3-amino[2]staffane hydrochloride (*I*, n = 2, X = H, Y = NH_3Cl, 190 mg, 95% pure according to the ^1H NMR spectrum). To the mixture of the crude hydrochloride (190 mg), chloroform (0.17 g, 1.4 mmol) and benzyltriethylammonium chloride (10 mg, 0.4 mmol) in dichloromethane (1 ml), 50% aqueous sodium hydroxide solution (0.5 ml) was added in one portion, and the mixture was stirred at room temperature for 3 h. Then more water (2 ml) was added, the product was extracted with dichloromethane (3 × 5 ml), and the dichloromethane phase was washed with water and dried. Evaporation of the solvent yielded crude product which was purified by silica gel column chromatography with $CHCl_3$ as an eluent, then followed by sublimation (50 °C/25 mm Hg) to give pure [2]staffane-3-isonitrile (*I*, n = 2, X = H, Y = NC, 60 mg, 27% yield based on [2]staffane-3-carboxylic acid), m.p. 121 °C. ^1H NMR spectrum: 1.63 (s, 6 H); 2.00 (s, 6 H); 2.40 (s, 1 H). ^{13}C NMR spectrum: 26.81, 37.42, 40.55 (t, J = 6), 42.89, 49.50, 54.17, 155.34. IR spectrum: 2 138, 2 123 (NC). MS, *m/z* (rel. int., %): 159 (M, 1.3), 132 (19), 117 (37), 91 (44), 77 (19), 39 (27). For $C_{11}H_{13}N$ (159.2) calculated: 82.97% C, 8.23% H, 8.80% N; found: 82.90% C, 8.21% H, 8.75% N. HR MS (EI), *m/z*: 159.1017, (calculated for $C_{11}H_{13}N$ 159.1048).

A small amount of the hydrochloride salt of 3-amino[2]staffane (*I*, n = 2, X = H, Y = NH_3Cl) was converted to the free 3-amino[2]staffane (*I*, n = 2, X = H, Y = NH_2), which was sublimed (50 °C/25 mm Hg), m.p. 68 °C. ^1H NMR spectrum: 1.57 (s, 6 H); 1.59 (s, 6 H); 1.63 (s, 3 H); 2.39 (s, 1 H). ^{13}C NMR spectrum: 26.55, 34.04, 44.28, 48.10, 49.48, 52.37. IR spectrum: 3 390, 3 320 (NH). MS, *m/z* (rel. int., %): 149 (M, 10), 148 (28), 108 (52), 93 (44), 91 (61), 82 (39), 42 (63). HR MS (CI), *m/z*: 150.1293; (calculated for $C_{10}H_{16}N$ 150.1283).

This sample was quite hygroscopic and a satisfactory elemental analysis was not obtained.

μ-([1]Staffane-1,3-diisocyanide-C,C')bis(pentacarbonylmolybdenum) (*XVIII*)

A solution of the diisonitrile *XIV* (75 mg, 0.63 mmol) and molybdenum hexacarbonyl (3.3 g, 12.6 mmol) in THF (130 ml) was stirred and irradiated in a quartz tube for 20 min with a 450 W medium pressure Hanovia mercury lamp under argon. Solvent was evaporated and excess molybdenum hexacarbonyl was removed by sublimation (50 °C/3 mm Hg). Residue was extracted with chloroform (4 × 15 ml) and combined extracts were filtered through a silica gel bed. Evaporation of the chloroform gave *XX* in 85% yield (0.27 g), as estimated from the ^1H NMR spectrum. Less soluble impurities were removed by several crystallizations from chloroform and from a chloroform–hexane (2 : 1) mixture. Mother liquid from the last crystallization was concentrated and the residue washed with hexane to give pure *XVIII* (70 mg, 19%), m.p. 130 °C (dec.). ^1H NMR spectrum: 2.82 (s). ^{13}C NMR spectrum: 41.17, 60.56, 203.30, 205.22. IR spectrum: 2 140 (NC), 2 055, 2 008, 1 989, 1 958, 1 925, 1 914 (CO). CI MS, *m/z* (rel. int., %): 595 (2), 594 (3), 593 (4), 592 (4), 591 (6), 590 (3), 589 (3), 588 (3), 586 (2), 266 (90), 265 (100). For $C_{17}H_6No_2N_2O_{10}$ (590.1) calculated: 34.60% C, 1.02% H, 4.75% N; found: 34.43% C, 1.07% H, 4.71% N.

TABLE IV
Crystal data, data collection conditions, and solution and refinement details for $C_{30}H_{38}N_2O_8Rh_2 \cdot 6\ CHCl_3$

Crystal data	
Formula	$C_{36}H_{44}N_2O_8Rh_2Cl_{18}$
Color; habit	clear red plates
Crystal dimensions, mm	0.1 × 0.4 × 0.5
Space group[a]	$P2_1/c$
Crystal system	monoclinic
Unit cell dimensions[b,c]; Å, °	a = 13.998(3), b = 11.220(3), c = 18.542(4), β = 95.39(2)
Volume, Å^3	2 899.3(12)
Formula units / cell	Z = 2
Formula weight, a.m.u.	1 476.7
Density (calc.), g cm^{-3}	1.691
Absorption coefficient, mm^{-1}	1.442
F(000)	1 468

Data collection	
Diffractometer used	Siemens P3/F
Radiation	MoKα (λ = 0.71073 Å)
Temperature, °C	−135
Monochromator	highly oriented graphite crystal
Mosaic character[d], °	0.60
2θ range, °	3.0 to 45.0
Scan type	ω
Scan speed, °/min	variable; 3.91 to 58.59
Scan range, °	from 0.80 below 2θ for Kα1 to 0.80 above 2θ for Kα2
Background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 50% of total scan time
Standard reflections	4 measured every 96 reflections
Index ranges	$-15 \le h \le 3$, $-2 \le k \le 12$, $-19 \le l \le 19$
Reflections collected	6 446
Unique reflections[e]	3 779 (R_{int} = 3.98%)
Observed reflections	2 943 ($F > 4.0\ \sigma(F)$)
Absorption correction	*n/a*

TABLE IV
(*Continued*)

Solution and refinement	
System used[f]	Siemens SHELXTL PLUS (MicroVAX II)
Solution	direct methods
Refinement method[g]	full-matrix least-squares
Scattering factors	neutral atoms[h]
Extinction correction	*n/a*
Hydrogen atoms[i]	riding model, refined isotropic *U*
Weighting scheme	$w = 1.0/(\sigma^2(F) + 0.0009\,F^2)$
Final residuals (obs. data), %	$R = 5.23$, $wR = 6.47$
Residuals (all data), %	$R = 6.73$, $wR = 6.90$
Goodness-of-fit	1.43
Largest and mean Δ/σ	0.002, 0.000
Data-to-parameter ratio	9.7 : 1
Largest difference peak, e/Å^3	1.12
Largest difference hole, e/Å^3	−1.16

[a] *International Tables for X-Ray Crystallography*, Vol. A. D. Reidel Publishing, Dordrecht/Boston 1983; [b] cell dimensions were determined by least-squares fit of the setting angles for 25 reflections with 2θ in the range 34.1 – 41.9°. Angle tolerances for centering, 2θ, ω and χ: 0.02, 0.01, and 0.05; [c] estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables; [d] crystal mosaic character was determined from the width at half height of ω scans; [e] $R_{int} = [\sum N(\sum w(F_{mean} - F)^2)/\sum(N-1)\sum wF^2]^{1/2}$; [f] Sheldrick G. M.: *SHELXTL-PLUS. A Program for Crystal Structure Determination*, Version 4.1. Siemens Analytical X-Ray Instruments, Madison 1990; [g] the quantity minimized in the least-squares procedures is: $\sum w(|F_o| - |F_c|)^2$, $R = R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR = R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$; [h] *International Tables for X-Ray Crystallography*, Vol. 4. Kynoch Press, Birmingham 1974; [i] methyl hydrogen atoms were treated as rigid groups free to rotate about the attaching C–C bond.

μ-([2]Staffane-3,3′-diisonitrile-C,C′)bis(pentacarbonylmolybdenum) (*XIX*)

This complex was prepared from the diisonitrile *XV* (80 mg, 0.43 mmol) as described above. Because of low solubility of the product in organic solvents, the residue left after removal of molybdenum hexacarbonyl by sublimation was extracted with a larger amount of chloroform (4 × 40 ml) to give *XIX* in 90% yield (150 mg). Purification as described above gave a pure product (40 mg, 14%), m.p. > 120 °C (dec.). ^{1}H NMR spectrum: 2.17 (s). ^{13}C NMR spectrum: 35.62, 42.19, 55.10, 200.99, 203.62, 206.03. IR spectrum: 2 158 (NC), 2 065, 1 986, 1 959, 1 916 (CO). CI MS, *m/z* (rel. int., %): 661 (0.3), 660 (0.2), 659 (0.3), 658 (0.3), 657 (0.4), 655 (0.2), 654 (0.5), 653 (0.2), 652 (0.2), 651 (0.2), 650 (0.2), 649 (0.2), 266 (100), 265 (90). For $C_{22}H_{12}Mo_2N_2O_{10}$ (656.2) calculated: 40.26% C, 1.84% H, 4.27% N; found: 40.39% C, 2.02% H, 3.95% N.

Crystal of Bis([2]staffane-3-carbonitrile)dirhodium(II) Tetraacetate

This complex is formed after heating a $CHCl_3$ solution containing one equivalent of dirhodium(II) tetraacetate and two equivalents of [2]staffane-3-nitrile at 40 °C for 30 min. Deep violet plates of $Rh_2(O_2CCH_3)_4(NCC_{10}H_{13})_2$. 6 $CHCl_3$ were formed upon very slow evaporation of the solvent at room temperature. The crystals lose $CHCl_3$ very easily at room temperature.

TABLE V
Atomic coordinates[a] (. 10^4) and equivalent isotropic displacement parameters for $C_{30}H_{38}N_2O_8Rh_2$. 6 $CHCl_3$

Atom	*x/a*	*y/b*	*z/c*	U_{eq} (. 10^4), Å^{2}, [b]
Rh(1)	591(1)	59(1)	4578(1)	159(2)*
O(1)	-417(3)	-508(4)	3793(2)	202(15)*
O(2)	932(3)	-1661(4)	4808(2)	220(15)*
O(3)	1537(3)	610(4)	5414(2)	199(15)*
O(4)	190(3)	1790(4)	4409(2)	216(15)*
N(1)	1671(5)	132(5)	3789(3)	268(21)*
C(1)	-1259(5)	-717(6)	3959(4)	208(24)*
C(2)	475(5)	-2215(6)	5250(4)	187(22)*
C(3)	-1971(6)	-1129(8)	3356(4)	348(27)*
C(4)	714(6)	-3521(6)	5393(5)	325(26)*
C(5)	2224(6)	145(6)	3377(4)	265(24)*
C(6)	2950(5)	172(7)	2870(4)	252(24)*
C(7)	3713(6)	1150(7)	2804(4)	358(28)*
C(8)	2802(5)	166(8)	2033(4)	340(26)*
C(9)	3748(6)	-763(7)	2804(5)	363(29)*
C(10)	3899(5)	198(6)	2231(4)	241(23)*
C(11)	4687(5)	221(6)	1738(4)	258(24)*
C(12)	4928(6)	1242(9)	1219(5)	512(34)*
C(13)	4861(7)	-636(9)	1123(5)	569(38)*
C(14)	5776(6)	172(9)	1971(5)	520(35)*
C(15)	5682(6)	269(8)	1146(5)	382(29)*
C(16)	730(6)	-2758(7)	3125(4)	368(28)*
Cl(1)	364(3)	-2316(4)	2254(2)	1226(19)*
Cl(2)	-72(2)	-3813(3)	3410(2)	787(12)*
Cl(3)	1895(2)	-3289(2)	3187(2)	665(10)*
C(17)	3241(6)	-1180(8)	5434(4)	436(31)*
Cl(4)	3537(3)	-2178(4)	4779(2)	1196(18)*
Cl(5)	2857(2)	-1915(2)	6187(1)	524(8)*
Cl(6)	4232(2)	-286(3)	5722(2)	1004(15)*
C(18)	2292(6)	2817(7)	4504(4)	324(27)*
Cl(7)	3450(2)	2213(2)	4611(1)	429(7)*
Cl(8)	2157(2)	3854(2)	5198(1)	581(9)*
Cl(9)	2066(2)	3472(2)	3654(1)	561(9)*

TABLE V
(*Continued*)

Atom	*x/a*	*y/b*	*z/c*	U_{eq} (. 10^4), $Å^{2,b}$
H(3A)	-2549	-1463	3511	354
H(3B)	-1692	-1682	3040	1070
H(3C)	-2116	-397	3102	1117
H(4A)	132	-3977	5375	972
H(4B)	1075	-3633	5854	699
H(4C)	1089	-3781	5015	1054
H(7A)	4198	1216	3204	551
H(7B)	3478	1908	2624	725
H(8A)	2528	880	1815	390
H(8B)	2544	-549	1807	262
H(9A)	3542	-1532	2624	316
H(9B)	4236	-804	3204	180
H(12A)	5153	1975	1442	749
H(12B)	4474	1359	804	1285
H(13A)	4406	-628	702	1395
H(13B)	5051	-1426	1275	863
H(14A)	6015	-573	2168	306
H(14B)	6045	852	2231	896
H(15)	6194	293	836	328
H(16)	710	-2068	3429	288
H(17)	2734	-672	5229	498
H(18)	1834	2189	4543	164

[a] Atoms have occupancies of 1.0. [b] For atoms marked with *, the equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

X-Ray Diffraction Data Collection and Crystal Structure Determination

A crystal of approximate dimensions 0.1 × 0.4 × 0.5 mm was used in the X-ray diffraction study. The diffraction data were collected at -135 °C on a Siemens P3/F diffractometer using graphite-monochromatized MoKα radiation (λ = 0.71073 Å). A total of 6 446 reflections were collected using an ω-scan.

The crystal structure was determined by the direct method and subsequent fullmatrix least-squares refinement. Final R and wR values are listed in Table IV. All pertinent atomic coordinates and equivalent isotropic displacement parameters are summarized in Table V. The structural calculation was done on a Siemens (Micro VAX II) system using the SHELXTL PLUS program.

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