Coordination chemistry of perhalogenated cyclopentadienes and alkynes, XXIII

The reaction of dichloroethyne with Ni(0) phosphine complexes: the strong influences of phosphine, solvent and concentration on the product composition. Structures of $Ni(PPh_3)_2(Cl)(C\equiv CCl)$ and $[Ni(PBu_3)_2(C\equiv C-PBu_3)_2]^{2+}[SbF_6^-]_2$

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Abstract

Dichloroethyne reacts with $[Ni(PR_3)_2(C_2H_4)]$ (R=Ph, Me, Et, Pr, Bu) or $[Ni(dcpe)(C_2H_4)]$ (dcpe=bis-dicyclohexylphosphinoethane) to form the π-complexes $Ni(PR_3)_2(\eta-ClC\equiv CCl)$, the σ-alkynyl complexes $[Ni(Cl)(C\equiv CCl)(PR_3)_2]$, the phosphonioacetylide complexes $[NiCl(C\equiv C-PR_3)(PR_3)_2]Cl$, or the cyclotrimerization products $[NiCl_2(C_6Cl_4PR_3)(PR_3)]$ depending on both the nature of the phosphine and the reaction conditions. In the phosphonioacetylide complexes, one chloride can easily be substituted by other anions, while the addition of two equivalents of $AgSbF_6$ results in the formation of the first examples of the bis-(phosphonioacetylide) complexes $[Ni(C\equiv C-PR_3)_2(PR_3)_2]^{2+}[SbF_6^-]_2$. The structures of $[Ni(Cl)(C\equiv CCl)(PPh_3)_2]$ and $[Ni(C\equiv CPBu_3)_2(PBu_3)_2][SbF_6]_2$ have been determined by X-ray diffraction. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Nickel complexes; Dichloroethyne; Alkyne complexes; Phosphonioacetylide complexes; Mechanism

1. Introduction

Since the discovery of the nickel catalyzed cyclotetramerization of ethyne to cyclooctatetraene by Reppe nearly 50 years ago [1], numerous studies have shown that the result of the interaction of alkynes with nickel complexes strongly depends on the nature of the ligands bonded to nickel, and the substituents at the triple bond as well as on the reaction conditions. Besides a large number of catalytic processes, also a variety of stoichiometric reactions leading to 'simple' π-complexes, or more complicated cyclooligomerization derivatives, have been discovered [2–7]. In the course of our studies on the coordination chemistry of dichloroethyne, we have already examined the reactions of this highly reactive alkyne with Pt(0) and Pd(0) phosphine complexes [8–10] where we observed either the formation of π-complexes $[Pt(PR_3)_2(\eta-ClC\equiv CCl)]$, the oxidative

addition of one C–Cl bond to give the σ-chloroethynyl complexes $[Pt(Cl)(C\equiv CCl)(PR_3)_2]$ or the surprising formation of the phosphonioethynyl complex *cis*-$[PdCl_2(C\equiv C-PPh_3)(PPh_3)]$. In view of the many exciting results obtained with Ni(0) complexes and other alkynes, we decided that it would be worth while to look also at the reactions of the Ni(0) phosphine complexes '$[Ni(PR_3)_2(C_2H_4)]$' with dichloroethyne.

There are usually three different approaches used for the synthesis of the π-alkyne derivatives of Ni(0) phosphine complexes [11–13]:

(a) treatment of Ni(0)–olefin complexes like $[Ni(COD)_2]$ with the appropriate phosphine, followed by addition of the alkyne;
(b) reaction of $[Ni(PR_3)_4]$ with the alkyne; or
(c) substitution of ethylene in the complexes $[Ni(PR_3)_2(C_2H_4)]$ (**1**) by the alkyne.

Because of the known high reactivity of $ClC\equiv CCl$ towards

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phosphines [14], the first two strategies were expected to result in undesired side reactions occurring, which implies the presence of free phosphines, and therefore we investigated strategy (c). While the ethylene complexes [Ni(dcpe)(C_2H_4)] (**1b**)[1] and [Ni(PPh$_3$)$_2$(C_2H_4)] (**1c**) can be prepared quite easily [15,16], there appears to be no straightforward procedure for the preparation of the alkyl phosphine derivatives [17]. Ni(0) phosphine complexes with these ligands have been prepared previously by in situ Na or Zn reduction of the corresponding dihalides [NiX$_2$(PR$_3$)$_2$] under argon [18–20]. Therefore, it was considered likely that by performing these reductions under an ethylene atmosphere the desired olefin complexes [Ni(PR$_3$)$_2$(C_2H_4)] with R=Me (**1d**), Pr (**1e**), ^{n}Bu (**1a**) may be generated in situ. This could be verified by the isolation of **1a** from hexane solutions at low temperature.

Therefore, we examined the reactions of ClC≡CCl with either the isolated complexes **1a**–**c** or the (filtered) reduction solutions of **1a**, **d** and **e**. We soon learned that not only the choice of phosphine, but also the solvent, strongly influenced the nature of the products.

2. Results

2.1. Reactions of **1a**–**c** in hexane or Et$_2$O

Treatment of a solution of **1a** in hexane at −78°C with an approximately equimolar amount of an Et$_2$O solution of ClC≡CCl leads to the formation of a yellow powder in high yield. The spectroscopic (IR, ^{1}H, ^{13}C, ^{31}P-NMR, see Table 1) data indicates that this product is the π-ClC≡CCl complex [Ni(PBu$_3$)$_2$(η-ClC≡CCl)], **2a** (compare Refs. [9,13]). A product with similar spectroscopic data was also
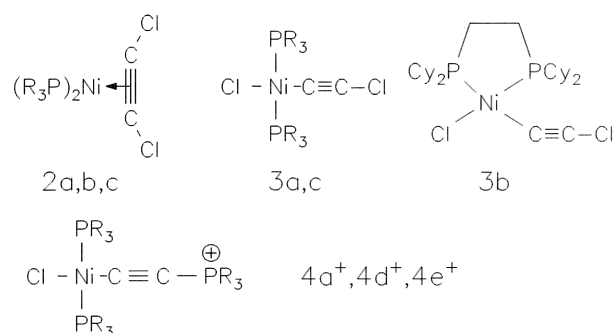
obtained from the reaction of [Ni(dcpe)(C_2H_4)] (**1b**) with ClC≡CCl at low temperature (<−25°C) in Et$_2$O, and is therefore most likely the dcpe analog of **2a**.

Heating a hexane solution of **2a** at 40°C for 1 h produces the new product **3a**. Elemental analysis suggests that this is an isomer of **2a**, and we conclude from the ^{13}C-NMR data (Table 1) by comparison with the Pt analogue, that **3a** is the σ-alkynyl complex trans-[Ni-(Cl)(C≡CCl)(PBu$_3$)$_2$] (Chart 1). Stirring a CH_2Cl_2 solution of **2b** at r.t. for 2 h also produces a new species, which shows an AX pattern in its ^{31}P-NMR spectrum, which we attribute to the cis-chloro-alkynyl complex **3b**, [Ni(Cl)(C≡CCl)(dcpe)]. While in solution the π-complex is

Chart 1.

Table 1
IR and NMR spectroscopic data

Compound	IR [cm^{-1}]^a	$\delta(^{31}P)$ [ppm]^a	$J_{PP'}$ [Hz]	$\delta(^{13}C≡C)$ [ppm]/J [Hz]^a
2a	830 (C–Cl)	21.8 (H)		113.8m [N=90 Hz]
2b	822 (C–Cl)	81.2 (T)		–
2c	830 (C–Cl)	41.8 (T)		–
3a		8.4 (B)		79.1s, 70.4t [53]
3b		85.3d, 73.6d (M)	45	–
3c		21.6 (T)		–
X		19.3t [P_A], −6.8dd [$P_{M'}$], −3.8t [P_X]	$J_{AM}=2$, $J_{MX}=6$	
4a$^+$ Cl$^-$	2032	11.7d, 9.8t (A)	6	147.2dt [13/44 Hz], 95.0d [144] (A)
4d$^+$	2036	17.9t, −13.3d (A)	2	–
4e$^+$	2033	10.3d, 6.8t (A)	6	
5	2023	16.1t, 9.7t (A)	5	
6		37.5d, −9.2d (B) 41.0d, −8.4d (A)	17	174.6dd [110/29 Hz], 142.5d [24], 133.6s, 131.2t [12], 121.2s, 120.2s
7		36.6d, 1.9d (A)	3	
8$^+$		38.9 (A)		

^{a} IR spectra: $\nu_{(C≡C)}$, unless indicated otherwise. ^{13}C-NMR spectra always recorded in C$_6$D$_6$, unless indicated otherwise. ^{31}P-NMR spectra recorded in: (H)=hexane, (T)=toluene, (M)=CH_2Cl_2, (A)=acetone, (B)=C$_6$D$_6$.

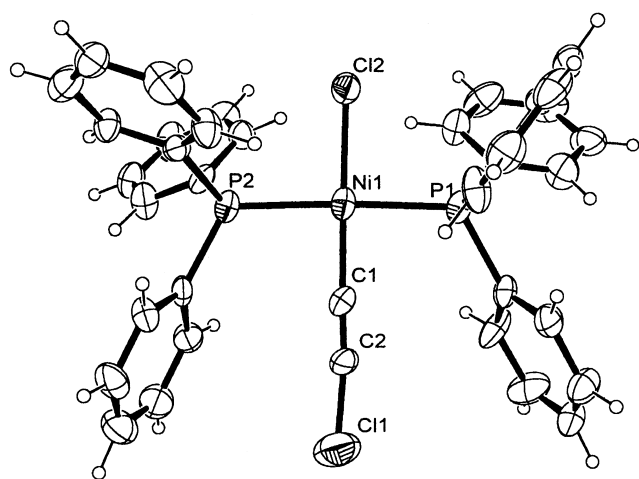^{1}dcpe = 1,2-bis-dicyclohexylphosphino-ethane.

Fig. 1. Molecular structure of **3c**. Thermal ellipsoids drawn at the 30% probability level. Selected distances [Å] and angles [°]: Ni1–C1 1.846(16), Ni1–Cl2 2.197(4), Ni1–P1 2.221(4), Ni1–P2 2.231(4), C1–C2 1.156(17), C2–Cl1 1.663(17); C1–Ni1–Cl2 174.2(4), P1–Ni1–P2 175.36(14), C2–C1–Ni1 175.2(13), C1–C2–Cl1 173.4(14).

still present, and complete isomerisation to **3b** cannot be achieved without concomitant decomposition.

The triphenylphosphine complex **1c** reacts with ClC≡CCl in Et_2O at low temperature ($<-20°C$) to form a 40:60 mixture (^{31}P-NMR) of two compounds. Heating a toluene solution of this mixture at 30–40°C for 1 h leads to the disappearance of one signal, and from this solution, after recrystallization, orange–yellow crystals can be obtained. X-ray diffraction characterized this compound as the σ-alkynyl complex *trans*-[Ni(Cl)(C≡CCl)(PPh$_3$)$_2$] (**3c**). Comparison with the former two reactions, as well as with the ^{31}P-NMR data of other π-alkyne complexes of the Ni(PPh$_3$)$_2$ fragment [13,21], identifies the minor component of the original reaction mixture as [Ni(PPh$_3$)$_2$(η-ClC≡CCl)] (**2c**).

2.2. Crystal structure determination of *3c* (Fig. 1, Table 2)

The cell parameters of **3c** are very similar to the analogous platinum complex, which we described some 10 years ago [8]. The cell volume is only 2% smaller than in the Pt complex. The molecular parameters are also very similar: the bond lengths and angles within the C≡C–Cl moiety are identical within the standard deviations, and the Ni–P and Ni–C distances are approximately 0.10 Å shorter than in the Pt analogue, as might be expected from the difference in covalence radii of Ni and Pt (0.12 Å). Only the Ni–Cl distance is significantly shorter (0.18 Å) than the corresponding Pt–Cl distance.

Table 2
Crystallographic data

	3c	5
Empirical formula	$C_{38}H_{30}Cl_2NiP_2$	$C_{52}H_{108}F_{12}NiP_4Sb_2$
Temperature / K	293(2)	193(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a [Å]	11.942(5)	21.073(8)
b	24.791(10)	13.153(11)
c	12.214(3)	25.554(8)
β [°]	114.96(2)	108.70(3)
Volume [Å^3]	3278(2)	6709(7)
Z	4	4
Density (calculated) [g cm^{-3}]	1.374	1.374
Crystal colour/habit	Orange/irregular fragment	Red–orange/prism
Crystal size	0.36×0.25×0.18 mm	0.35×0.28×0.15 mm
Diffractometer	SYNTEX R3	SYNTEX R3
Wavelength [Å]	0.71069	0.71069
Data collection method	ω-scan	ω-scan
2θ range [°]/completeness	4.0 to 40.2/81.7%	4.0 to 45.1/62.1%
Index ranges	±h, +k, +l	+h, +k, ±l
Reflections collected	2635	6082
Independent reflections	2635	5782 [R(int)=0.0318]
Structure solution/refinement	SHELXTL 4.11/SHELX 93	SHELX 93
Data/restraints/parameters	2635/0/388	5777/57/677
Goodness-of-fit on F^2 [a]	1.134	1.026
R_1 [$I > 2\sigma I$)] [a]	0.0700	0.0541
wR_2 (all data) [a]	(0.2404)	0.1389
Largest diff. peak and hole [e Å^{-3}]	0.791 and −0.481	0.690 and −0.478

[a] $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]\}^{1/2}$; $R_1 = \Sigma \|F_o| - |F_c\|/\Sigma |F_o|$; GooF $= S = \{\Sigma [w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; where P is $[2F_c^2 + \max(F_o^2, 0)]/3$.

2.3. Reactions in THF

When the reduction solutions, obtained from $[NiCl_2(PR_3)_2]$ (R=Me, Pr) and zinc under ethylene, are treated with $ClC{\equiv}CCl$, a mixture of several products is obtained. In both cases, after chromatography on silica gel, one major component can be isolated. Recrystallization from MeOH with the addition of $NaBPh_4$, produces microcrystalline products with similar spectroscopic properties. The spectroscopic data are similar to those of the phosphonioethynyl complexes $L_nM{-}C{\equiv}C{-}PR_3$ (M=Rh, Pd, Pt [10]), and elemental analyses suggest a formulation as '$[NiCl(C{\equiv}C{-}PR_3)(PR_3)_2]^+(BPh_4^-)$', (R=Me, $4d^+BPh_4^-$ and R=Pr, $4e^+BPh_4^-$).

The original product most likely contains chloride instead of tetraphenylborate, and with the known tendency of nickel–PMe$_3$ complexes to form trigonal bipyramidal species [22], both chlorides might be bound to the nickel atom. In acetone it seems very likely that the compound is ionic, perhaps with coordinated solvent [23]. There is also an impurity X in the ^{31}P-NMR spectrum of $4d^+$, which shows a typical AM_2X pattern, as might be explained by a trigonal bipyramidal structure as depicted in Scheme 1.

2.4. Reactions in toluene

(a) When a concentrated toluene solution of **1a** (0.38 mol l^{-1}) is treated with a $ClC{\equiv}CCl$ solution at room temperature, two main products can be isolated by chromatography: One is the σ-ethynyl complex **3a** (40% yield), the other shows similar spectroscopic features to those observed for $4d^+$ and $4e^+$, and is therefore most likely to be the phosphonioacetylide complex $[Ni(Cl)(C{\equiv}C{-}PBu_3)(PBu_3)_2]^+Cl^-$, ($4a^+Cl^-$) (Table 1).

Interestingly, the triplet ^{31}P-NMR signal associated with the phosphonium moiety is shifted by more than 8 ppm to lower field when the solvent is changed from acetone to toluene, while the other signal is not affected at all (shift 0.1 ppm). Although this might simply be due to the change in polarity of the solvent, we think this shift indicates coordination of the second chloride to the nickel centre, in accordance with Scheme 1. One chloride can be substituted

by other anions like BPh_4^-, PF_6^-, ClO_4^- through simple metathesis reactions with the corresponding sodium or ammonium salts. The ^{31}P-NMR spectra of these ionic species look very similar to the spectrum of $4a^+Cl^-$ in acetone, thus suggesting a similar structure.

If exactly one equivalent of $AgSbF_6$ is added to an ethanolic solution of $4a^+Cl^-$, the corresponding SbF_6^- salt can be isolated. However, if this reaction is performed with an excess of the silver salt, a new compound is formed. The IR spectrum shows a $\nu_{(C{\equiv}C)}$ band at 2023 cm^{-1} and a strong, broad $\nu_{(SbF)}$ band at 654 cm^{-1}, indicating still an ionic phosphonium acetylide species. The ^{31}P-NMR spectrum exhibits an A_2X_2 pattern, which suggests a formulation as the *trans*-bis-(phosphonium acetylide) complex $[Ni(C{\equiv}C{-}PBu_3)_2(PBu_3)_2]^{2+}(SbF_6^-)_2$ (**5**) Fortunately, it was possible to obtain X-ray quality crystals, and the structure determination confirmed the suggested structure (see below).

2.5. Molecular structure of $[Ni(C{\equiv}C{-}PBu_3)_2(PBu_3)_2]^{2+}(SbF_6^-)_2$ **5** (Fig. 2)

The two C–C triple bonds have the same lengths within 1σ and are slightly longer (0.055 Å, 4σ) than the C–C bond in **3c**, but quite 'normal' when compared to other known nickel bis-alkynyl complexes (1.22 Å [24]). On the other hand, the Ni–C bond lengths are (within 1σ) the same as in **3c**, but slightly shorter when compared to the published structures of bis(arylethynyl) nickel complexes (1.86–1.88 Å [24]). The angles at both carbon atoms of the triple bonds deviate slightly from linearity, which is quite a usual feature of all alkynyl complexes [24]. One of the two SbF_6 anions is severely disordered, while the other 'behaves' itself.

(b) In a second experiment we treated a highly concentrated toluene solution of **1a** (0.67 mol l^{-1}) with $ClC{\equiv}CCl$. A ^{31}P-NMR examination of the crude reaction product showed the presence of **3a**, $4a^+Cl^-$ and PBu_3O together with two AX spin systems and several weak unidentified singlets. After chromatographic work up a faint red product, **6**, could be isolated. The ^{31}P-NMR spectrum shows only one of the original two AX spin systems
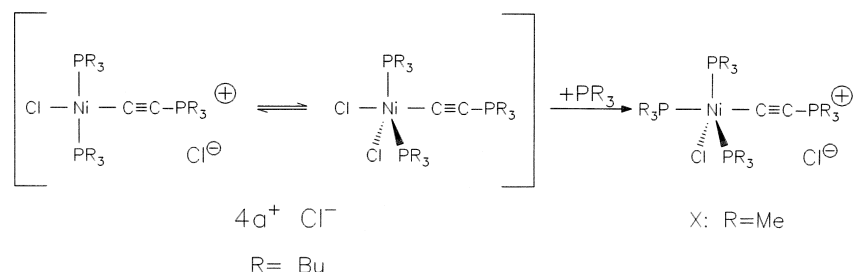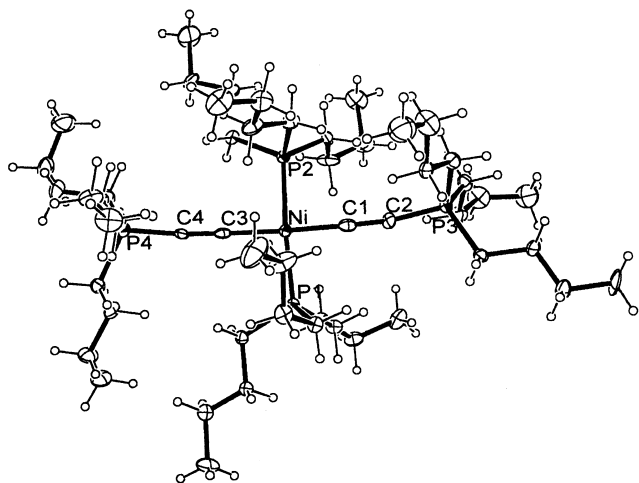

Scheme 1.

Fig. 2. Molecular structure of **5**. Thermal ellipsoids drawn at the 30% probability level. Selected distances [Å] and angles [°]: Ni–C1 1.832(12), Ni–C3 1.847(12), Ni–P1 2.207(3), Ni–P2 2.214(3), C1–C2 1.217(13), C2–P3 1.725(11), C3–C4 1.206(13), C4–P4 1.719(12); C1–Ni–C3 172.5(5), P1–Ni–P2 174.4(2), C2–C1–Ni 177.4(11), C1–C2–P3 171.9(9), C4–C3–Ni 176.6(10), C3–C4–P4 175.0(8).

(Table 1) and suggests the presence of two chemically very different phosphanes. The FAB-mass spectrum showed a molecular ion corresponding to 'Ni(PBu$_3$)$_2$C$_6$Cl$_6$', which also agreed with the elemental analysis data and suggests that this product results from a trimerization of ClC≡CCl. Since the IR spectrum shows no absorptions in the 2000–2200 cm^{-1} region, a linear trimerization as observed by Klein in his reactions of Ni–(PMe$_3$) complexes with monohalogenoalkynes [25], can be excluded. However, there are at least two further structures known as a result of cyclotrimerization reactions on Ni(0):

• nickelacycloheptatrienes [26–29]
• π-benzene complexes of Ni(0) [30,31]

Cyclotrimerization of ClC≡CCl usually gives hexachlorobenzene [32], which is known to undergo oxidative addition to Ni(0) to yield σ-*tetra*-chlorophenyl complexes [Ni(Cl)(C$_6$Cl$_4$H)(PR$_3$)$_2$] (R=Et [33] or ^{n}Bu [34]). Since

one of the phosphines in **6** has a low field ^{31}P resonance typical for phosphonium species ($\delta \approx 35$–40 ppm) and the size of the P–P coupling constant is in the range usually observed for $^3J_{PP}$ in nickel phosphine complexes that also contain phosphonium moieties,[2] the following three structural proposals can be made (Chart 2).

In this context, the very interesting complex {Ni(Cl)[σ-C$_6$Cl$_4$(PEt$_2$)-2](PEt$_3$)$_2$}, which shows a $^4J_{PP}$ coupling constant of 28 Hz, should be mentioned. It was obtained among other products in the reaction of 'Ni(PEt$_3$)$_2$' with PEt$_2$(C$_6$Cl$_5$) [37], and therefore oxidative addition of the η-phenyl ligand in (A) to give (B) seems very likely.

The ^{13}C-NMR data (Table 1), especially the observed ^{13}C–^{31}P coupling constants, are in agreement with structure B. Unfortunately, there is no ^{13}C-NMR data available for either the nickelacycloheptatrienes, or for the above-mentioned σ-C$_6$Cl$_4$PEt$_2$ complex. However, 'non-aromatic' sp^2-carbons such as in vinyl phosphonium salts or σ-vinyl nickel phosphine complexes always appear to have very small $^2J_{(^{13}C–^{31}P)}$ and $^3J_{(^{13}C–^{31}P)}$ couplings [38–40,45], which are not observed in **6**.

Treatment of an acetone solution of **6** with an excess of NaClO$_4$ resulted in the isolation of a pink product. The ^{31}P-NMR spectrum (Table 1) showed an AX pattern, similar to the before-mentioned second AX component of the evaporated reaction mixture of **1a** and ClC≡CCl (see the Experimental section). It therefore seems reasonable to assume that one of the nickel bound chlorides in **6** is partially replaced by the polar solvent, i.e. acetone, giving an ionic species, and that this ionization process is completed by the addition of NaClO$_4$ to give [Ni(Cl)(C$_6$Cl$_4$PBu$_3$)(PBu$_3$)(solv)]$^+$ClO$_4^-$ ('**7**$^+$ClO$_4^-$'). The change in the size of the P–P coupling constant also indicates a change in the geometry around nickel. Elemental analysis of **7** suggests that the coordinated solvent is lost upon drying under vacuum.

Similarly, the addition of AgSbF$_6$ to an acetone solution of **6** and the subsequent monitoring of the reaction by ^{31}P-NMR showed not only the formation of **7**$^+$SbF$_6^-$, but also of [Ag(PBu$_3$)$_x^+$]SbF$_6^-$, and an unknown compound

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[2]For example, $^3J_{(P–P)}$ in Cl(Me$_3$P)Ni–C(Ph)(PMe$_3$)–C(H)(COR) is 15 Hz [35], in Cl(Me$_3$P)Ni–C$_6$H$_4$–CMe$_2$CH(PMe$_3$) is 10 Hz [36].

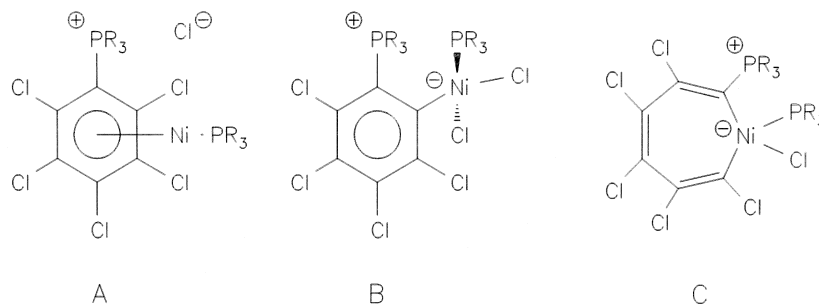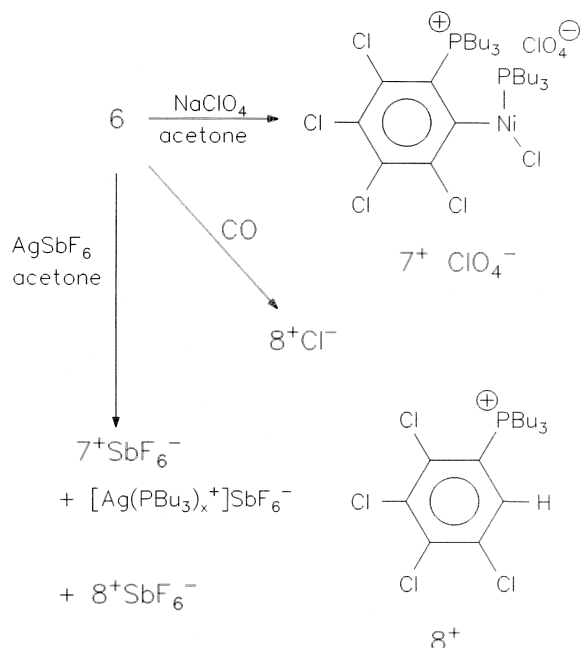Chart 2.

with a low field NMR signal at 38.9 ppm. From this mixture, an off-white product could be isolated that showed only the latter ^{31}P-NMR signal. Recrystallization yielded a small amount of X-ray diffraction quality crystals, which were consequently examined on the diffractometer. Quite surprisingly, it turned out that this product was the 2,3,4,5-tetrachlorphenylphosphonium salt [Bu_3P–C_6HCl_4]SbF_6 ($8^+SbF_6^-$). Treatment of **6** with CO produced a compound with similar spectroscopic features, suggesting its formulation as 8^+Cl^-. Both these results support the proposed formulation of complex **6** as a σ-phenyl complex (structure B in Chart 2).

The reactions of **6** are summarized in Scheme 2.

3. Discussion

Dichloroethyne reacts with Ni(0) phosphine complexes in a similar manner as with the Pd(0) and Pt(0) complexes examined by us previously, as is shown by the formation of the π-complex **2**, the σ-chloroethynyl complex **3** and the phosphoniumacetylide complex **4**. Additionally, dichloroethyne undergoes a cyclotrimerization reaction, not forming a simple derivative of hexachlorobenzene, however, but instead forming the tetrachlorophenylphosphonium species **6**.

Certainly, the primary reaction product is a π-complex **2**, which can be isolated at low temperatures. On warming, this π-complex isomerizes via oxidative addition to a σ-chloroethynyl complex **3**, presumably first as the *cis*-

isomer, which then quickly rearranges to the thermodynamically more favoured *trans*-isomer. Obviously, when pure ethene complexes such as **1** are used, the reaction does not proceed any further.

However, when in situ preparations of **1** are used, these σ-complexes undergo a sequence of reductive elimination and/or oxidative addition reactions, as has been postulated before to account for a nickel–carbon migration of a phenyl group in [Ni(C_6H_4R)(C(Cl)=CCl_2)(PMe_3)$_2$] [40], to give finally, the products **4** and/or **6**. Although it is known for a long time that the synthesis of phosphonium salts is catalyzed by nickel complexes [41–43], the formation of σ-alkynyl or phenyl phosphonium complexes has not been described before.

It has been postulated that Ni(I) species form on the sodium reduction of Ni(II) complexes in toluene solution [20], and it has also been shown that the reduction of NiX_2L_2 in the presence of acetylenes with Na/Hg can give Ni(I)–alkyne complexes, depending on the nature of L and the acetylene [44]. For MeOOC–C≡C–COOMe, on the other hand, only cyclotrimerization was achieved by reaction with [Ni(PPh_3)Cl]$_n$. As was mentioned before, the nickel catalyzed formation of phosphonium salts has been known for a long time. In an elegant mechanistic study, mainly centred on the formation of biaryls under the influence of nickel complexes, Kochi showed that the formation of arylphosphonium salts is also catalyzed by Ni(I) species [43]. Transferring Kochi's mechanism to our problem leads to the mechanism depicted in Scheme 3:

Either

(a) Cl–C≡C–Cl oxidatively adds to a Ni(I) complex NiCl(PR$_3$)$_n$ to give an intermediate Ni(III) complex T_1, which reductively eliminates Cl–C≡C–PR$_3^+$ Cl$^-$ with regeneration of Ni(I). The β-chloroethynylphosphonium cation might then oxidatively add to Ni(0), followed by nucleophilic displacement of the *trans*-phosphine ligand by chloride to give the intermediate Ni(II) complex T_2. This mechanism corresponds to the one postulated by us earlier for the formation of *cis*-[PdCl$_2$(C≡C–PPh$_3$)(PPh$_3$)] [10]. Here this intermediate, T_2, might then undergo a cycloaddition reaction with two molecules of Cl–C≡C–Cl to give directly the σ-phenyl complex **6**, or

(b) the chloroethynyl complex **3** adds oxidatively to the Ni(I) species, giving the intermediate Ni(II,III) complex T_3. The more reactive Ni(III) centre then reductively eliminates complex **4** with regeneration of Ni(I). The viability of this pathway could be shown by an independent reaction of **3a** with the reduction solution obtained from Na powder and [NiCl$_2$(PBu$_3$)$_2$], which gave a 35% yield of $4a^+Cl^-$.

The phenyl complexes **6** might in principal also be formed by a $2+2+2$ cycloaddition of dichloroethyne and chloro-
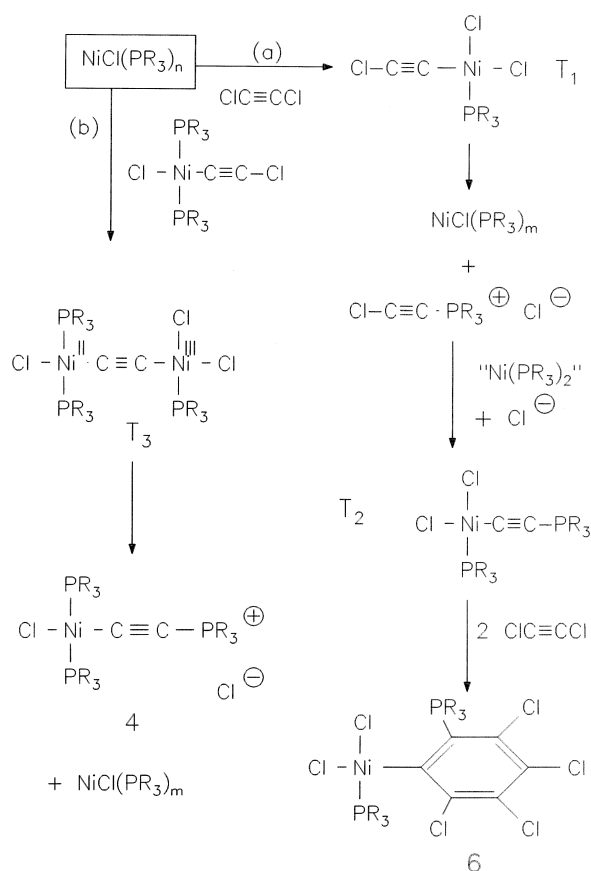
Scheme 2.

Scheme 3.

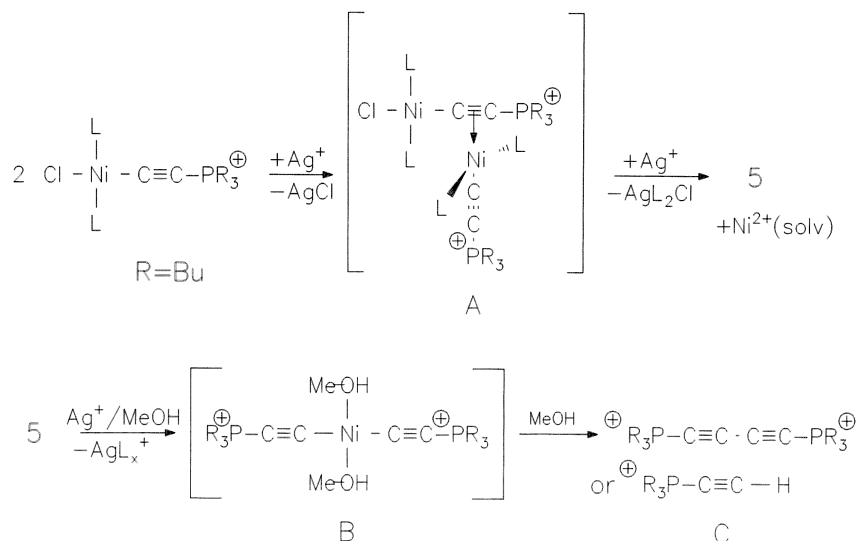The next part of the discussion is concerned with the reactivity studies of the phosphonium complexes **4** and **6**.

How can the formation of the bis(phosphonium ethynyl) complexes **5** be explained? Disproportionation reactions of the type:

$$2[Ni(X)(R')(PR_3)_2] \leftrightarrow [Ni(R')_2(PR_3)_2] + [NiX_2(PR_3)_2]$$
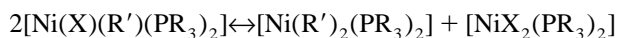
are known in nickel chemistry [45], and the formation of **5** might be just another example for such a reaction, with $R' = C \equiv C-PBu_3$. However, the question arises, which role is played by the silver ions?

> We therefore monitored this reaction by ^{31}P-NMR. It can be seen that the signals of **4a**$^+$ are gradually displaced by the signals of **5**, with concomitant formation of $[Ag(PBu_3)_x]SbF_6$. After standing for several days, only the broad signals of the latter species and a signal of an unknown compound at 18.5 ppm are left. An IR spectrum of this solution shows a medium strong absorption at 2072 cm^{-1}.

The observations of the NMR experiment indicate that the silver salt does not only abstract the nickel-bound chloride, but also attacks the phosphine ligands. It seems reasonable to assume that after the first chloride ions have been abstracted (and have most likely been replaced by the weakly coordinating solvent), the newly generated species attacks the starting material, forming an alkynyl-bridged intermediate **A** (Scheme 4). This intermediate is attacked by the silver salt which abstracts chloride and phosphine ligands from one nickel atom and induces the migration of the bridging alkynyl group to the other nickel atom, thus producing **5** together with solvated Ni^{2+}. If there is an even larger excess of AgSbF$_6$, then **5** also gets attacked with the formation of further $[Ag(PBu_3)_x^+]$ species, leaving

ethynylphosphonium chloride, followed by the oxidative addition of an aromatic C–Cl bond to Ni(0). However, the selective formation of only one isomer of **6** makes a pathway via route (a) more likely.

Scheme 4.

the nickel bis-phosphonium acetylide fragment **B**, which is then decomposed by MeOH to give other phosphonium species **C**, e.g. $[Bu_3P–C≡CH]^+$, or $[Bu_3P–C≡C–C≡C–PBu_3]^{2+}$ as products of hydrolysis or of reductive elimination,[3] to which we assign the NMR signal at 18 ppm and the IR band at 2072 cm^{-1}.

Such a silver-induced decomposition of Ni(II) phosphine complexes has precedent. Wada et al. could show that $ArNiL_2'Cl$ ($L'=PPh_3$) was decomposed by Ag^+ to $[AgL_2']^+ + AgCl$ [47–49]. A stepwise degradation of $[NiBr(C_6F_5)(PPh_3)_2]$ by $AgClO_4$, similar to the one depicted in Scheme 4, was described in a ^{31}P-NMR study on the 'role of $AgClO_4$ in activating a σ-arylmetal halide complex for ethylene dimerisation' [50]. There is also the possibility that Ag^+ acts as an alkynyl transfer reagent between two nickel centres, similar to the role played by Cu(I) in the Pd complex catalyzed cross-coupling of alkynes with haloarenes [51,52].

These examples from the literature, particularly the Ag^+ induced decomposition of nickel–polyhalophenyl complexes [47–49], also explain the formation of **8** from **6** and $AgSbF_6$. Mechanistically, the originally formed cation **7**$^+$ might be unstable towards hydrolysis and yield **8**$^+$, according to:

$$[Ni(Cl)(C_6Cl_4PBu_3)(Bu_3P)]^+ + H_2O$$
$$\rightarrow \text{'}NiCl(OH)(PBu_3)\text{'} + [C_6Cl_4H(PBu_3)]^+$$
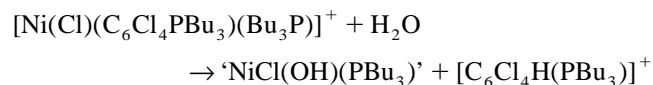
which corresponds to the decomposition pathway that was formulated in the high temperature reaction of PPh_3 with C_6F_5Br in the presence of $NiBr_2$, which resulted in the formation of $[Ph_3P(C_6F_4H)]^+Br^-$ [53]. The role of the Ag^+ may be abstraction of halide and phosphine from the nickel species, which might end up as the insoluble species $Ni(OH)_2$.

4. Experimental

Caution! Dichloroethyne is known to be neurotoxic and is suspected to be a carcinogen. In the pure state, it is also a highly explosive substance. Therefore, it should always be used as a Et_2O solution, and all work should be performed in a well-ventilated hood. Discarded reaction mixtures or washing liquids should be treated with ethanol solutions of iodine for several days before being disposed of.

The reactions described here were performed using standard Schlenk tube techniques, using argon-saturated absolute solvents, and argon as an inert gas. Dichloroethyne solutions were prepared according to the literature [54] and purified once by distillation. These solutions have an average concentration of approximately 3.5 molar and are termed 'standard solutions' in the following

experimental procedures. $Ni(PPh_3)_2(C_2H_4)$ (**1c**) and $Ni(dcpe)(C_2H_4)$ (**1b**) were prepared according to literature procedures [15,16]. The other Ni(0) complexes were always prepared in situ. However, the PBu_3 complex (**1a**) can also be isolated (see below).

NMR spectra were recorded on a JEOL GSX 270 spectrometer, IR spectra on a Perkin-Elmer model 881 and the FAB-MS spectrum on a Finnigan MAT 900. Elemental analyses were performed at the Institute of Inorganic Chemistry, University of Munich. The crystal structure determinations were performed on a Syntex-Nicolet R3 diffractometer, with MoKα radiation, in ω-scan mode. The structure determination of **6a** had to be performed at low temperature due to decomposition in the X-ray. As a consequence of the architecture of the low-temperature device no complete ψ-scans could be performed, which lead to an insufficient treatment of absorption phenomena, and thus no absorption corrections were applied.

4.1. Synthesis of $Ni(PBu_3)_2(C_2H_4)$ (**1a**)

$NiCl_2(PBu_3)_2$ [55,56] (1.39 g, 2.60 mmol) and sodium dust (0.42 g, 18.2 mmol) were stirred for 20 h in toluene under ethylene. The precipitate of NaCl and the unreacted Na dust were separated by centrifugation, and the yellowish solution evaporated in vacuo. The red oily residue was taken up in a minimum amount of pentane (saturated with ethylene) and cooled to $-78°C$. Small yellow–orange crystals of $Ni(PBu_3)_2(C_2H_4)$ formed (approx. 100 mg). ^{31}P-NMR (pentane): $δ=10.0$ ppm. ^1H-NMR (C_6D_6, Ar saturated): $δ=2.18$ (br, C_2H_4), 1.45 (br, $-(CH_2)_3-$), 0.91/0.81 (br, CH_3).

4.2. Synthesis of $Ni(PBu_3)_2(η-ClC≡CCl)$ (**2a**) and isomerization to $Ni(Cl)(C≡CCl)(PBu_3)_2$ (**3a**)

A suspension of Na dust (0.36 g, 15.7 mmol) in 9.0 ml toluene was treated with $NiCl_2(PBu_3)_2$ (1.56 g, 2.9 mmol) under ethylene. After stirring for 20 h, the suspension was filtered and the filtrate evaporated in vacuo. The remaining red oil was taken up in 5 ml hexane and, after cooling to $-78°C$, was treated with 0.83 ml of the 'standard $ClC≡CCl$ solution' (ca. 2.9 mmol). The solvent was evaporated at $-35°C$ in vacuo and the yellow residue was triturated with 5 ml pentane at $-78°C$, whereby a yellowish, slightly oily powder was isolated: **2a** (1.42 g, 88% yield).

Compound **2a** (0.92 g, 1.70 mmol) was dissolved in 10 ml hexane and was heated to $40°C$ for 1 h. Removal of the solvent in vacuo left a yellowish–brown residue which was then extracted with 15 ml of pentane. The extract was concentrated to about 50% of its original volume and then cooled to $-78°C$. A yellow powder precipitated, was isolated, and dried for 5 h in vacuo: **3a**. Yield 0.69 g (75%). $C_{26}H_{54}Cl_2NiP_2$ (558.2). Calc./found: C: 55.94/56.18; H: 9.75/9.95%.

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[3] The formation of 1,3-diynes from nickel bis-(σ-alkynyl) complexes, generated in situ, has been observed before [46].

4.3. Reaction of Ni(dcpe)(C₂H₄) (1b) with ClC≡CCl in Et₂O

A suspension of **1b** (0.30 g, 0.60 mmol) in 5 ml Et$_2$O was treated with 0.17 ml of the 'standard solution' (0.6 mmol) at -78°C. Stirring was continued at this temperature for 90 min, followed by removal of the solvent under vacuum at -25°C. A faint yellow powder was obtained after 2 h drying in vacuo at -25°C. A toluene solution of this product showed two ^{31}P-NMR signals. The minor component (ca. 10%) was unreacted starting material ($\delta =$ 49.0), the major signal at δ 81.2 ppm was assigned to **2b**.

After this powder was taken up in CH$_2$Cl$_2$ and stirred for 2 h at r.t., a ^{31}P-NMR spectrum showed again two sets of signals. The minor component (ca. 30%) was identified as unreacted **2b**, while the major component showed the typical AX pattern of an unsymmetrical *cis* complex, presumably **3b**. If stirring was continued, a jelly-like precipitate formed and the NMR spectrum showed only very broad signals. No satisfactory elemental analyses could be obtained, but the data are consistent with the proposed formulae.

4.4. Reaction of Ni(PPh₃)₂(C₂H₄) (1c) with ClC≡CCl in Et₂O

A yellow suspension of **1c** (2.37 g, 3.90 mmol) in 25 ml Et$_2$O was treated at -78°C with a 1.1 ml standard ClC≡CCl solution. With continuous stirring, the suspension was warmed to -40°C within 3 h. The temperature was then raised to -20°C and the solvent evaporated in vacuo. A light yellow powder was obtained. Its ^{31}P-NMR spectrum in toluene showed two signals at $\delta = 41.8$ (ca. 40%) and at $\delta = 21.6$ (ca. 60%). The low field signal was assigned to Ni(PPh$_3$)$_2$(η-ClC≡CCl) (**2c**) and the high field signal to *trans*-[Ni(Cl)(C≡CCl)(PPh$_3$)$_2$] (**3c**). This toluene solution was then heated to 30–40°C for 1 h. Hexane was then added until no more precipitate formed. The solid was isolated, washed with pentane and extracted with Et$_2$O. Slow cooling of the extract to -30°C yielded 0.42 g of yellow–orange crystals of **3c**, one of which was used for X-ray structure determination. C$_{38}$H$_{30}$Cl$_2$NiP$_2$·H$_2$O (695.7): Calc./found: C, 65.61/65.50; H, 4.64/4.61%.

4.5. Synthesis of [Ni(Cl)(C≡CPMe₃)(PMe₃)₂]⁺[BPh₄]⁻ (4d⁺BPh₄⁻)

NiCl$_2$(PMe$_3$)$_2$ (0.570 g, 2.00 mmol) and ca. 500 mg of powdered zinc were stirred in 5 ml THF under ethylene for 30 min. Centrifugation gave a clear yellow solution which was then cooled to -30°C and treated with 0.6 ml of the standard ClC≡CCl solution (ca. 2.0 mmol). The solution turned immediately black and was warmed to ambient temperature. After evaporation to dryness, the residue was taken up in Et$_2$O and chromatographed on silica gel. The first fraction with Et$_2$O was discarded. Further elution with

acetone gave an orange fraction, which was collected. Evaporation of the solvent yielded 224 mg of a yellowish brown oil. ^{31}P-NMR (acetone): $\delta = 18.2$s, -13.1s. IR: $\nu_{(C≡C)} = 2043$ cm^{-1}

This oil was dissolved in 6 ml MeOH and was treated with an excess of NaBPh$_4$. The ochre coloured precipitate was isolated and washed with several portions of MeOH, Et$_2$O and H$_2$O. After drying for 1 day in vacuo, 201 mg of **4d**$^+$BPh$_4^-$ (52% yield) was obtained. C$_{35}$H$_{47}$BClNiP$_3$ (665.6): Calc./found: C, 63.12/62.94; H, 7.11/7.04%.

4.6. Synthesis of [Ni(Cl)(C≡CPPr₃)(PPr₃)₂]⁺[BPh₄]⁻, 4e⁺BPh₄⁻

A solution of Ni(PPr$_3$)$_2$Cl$_2$ (2.00 g, 4.44 mmol) in 20 ml THF was treated with ca. 1 g powdered zinc and stirred for 24 h under ethylene. After filtration the dark yellow solution was cooled to -78°C and 1.3 ml standard ClC≡CCl solution (4.44 mmol) was added. Stirring was continued for 30 min at this temperature and for another 30 min at r.t. Evaporation of the solvent in vacuo resulted in a dark red viscous oil, which was taken up in Et$_2$O and chromatographed on silica gel. Elution with Et$_2$O gave a red fraction that was discarded. Acetone eluted a yellowish brown band that was collected. Evaporation of the solvent in vacuo gave 704 mg of a brown oil. ^{31}P-NMR (acetone): $\delta = 9.5$d [6 Hz], 7.2t [6 Hz]. IR: $\nu_{(C≡C)} = 2029$ cm^{-1}.

After dissolution of this oil in MeOH a saturated MeOH solution of NaBPh$_4$ was added, which precipitated an orange coloured powder. This product was isolated, washed with hexane and dried in vacuo. Yield: 1.80 g **4e**$^+$BPh$_4^-$ (44%). C$_{53}$H$_{83}$BClNiP$_3$ (918.0): Calc./found: C, 69.34/70.30; H, 9.11/9.09%.

4.7. Synthesis of [NiCl(C≡CPBu₃)(PBu₃)₂]Cl (4a⁺Cl⁻) and anion metathesis reactions

A mixture of NiCl$_2$(PBu$_3$)$_2$ (6.06 g, 11.3 mmol) and excess Na dust were suspended in 30 ml toluene and stirred for 40 h under ethylene. After centrifugation, the dark yellow solution was treated at -78°C with 3.3 ml standard ClC≡CCl solution (11.6 mmol). Stirring was continued for 15 min at this temperature and for 1 h at r.t. The solvent was then evaporated in vacuo. The dark yellow oily residue was taken up in 5 ml Et$_2$O and chromatographed on silica gel (2.5×15 cm, pretreated with pentane). Pentane (25 ml) eluted a yellow band, which after evaporation of the solvent gave 2.50 g **3a** (40%). Elution with Et$_2$O removed small amounts of residual **3a** from the column. Ethanol eluted a bright orange band that gave, after evaporation, 2.00 g of **4a**$^+$Cl$^-$ (46%) as a yellow powder. C$_{38}$H$_{81}$Cl$_2$NiP$_3$ (760.5): Calc./found: C, 60.01/59.69; H, 10.74/10.62%.

- A solution of **4a**$^+$Cl$^-$ (0.205 g, 0.27 mmol) in 5 ml EtOH/5 ml H$_2$O was treated with an excess of

NaBPh$_4$. A faint yellow precipitate was isolated after stirring for 15 min. Recrystallization from MeOH gave 219 mg **4a**$^+$BPh$_4^-$ (78%) as yellow needles.

$\delta(^{31}P)$ (acetone-d^6) = 11.0d, 7.3t (J_{PP} = 6 Hz)

C$_{62}$H$_{101}$BClNiP$_3$ (1044.3): Calc./found: C, 71.30/71.18; H, 9.75/9.80%.

- Stirring a solution of **4a**$^+$Cl$^-$ (0.187 g, 0.25 mmol) in 10 ml of a 1:1 EtOH/H$_2$O mixture with an excess of NH$_4$PF$_6$ for 30 min produced a yellow precipitate that was isolated and washed with 50 ml H$_2$O. Extraction with 3 ml Et$_2$O and cooling to −78°C gave 121 mg of **4a**$^+$PF$_6^-$ (57%) as a yellow powder.

$\delta(^{31}P)$ (acetone-d^6) = 11.8d, 8.3t (J_{PP} = 5 Hz)

C$_{38}$H$_{81}$ClF$_6$NiP$_4$ (870.0): Calc./found: C, 52.46/52.50; H, 9.38/9.35%.

- Addition of NaClO$_4$·H$_2$O (0.40 g, 2.9 mmol) to a solution of 110 mg of **4a**$^+$Cl$^-$ (0.15 mmol) in 4 ml EtOH produced a yellow solution, from which a flocculent yellow precipitate could be obtained by addition of 3 ml H$_2$O. After filtration and washing with several portions of water, the residue was recrystallized from a small amount of MeOH: 111 mg of **4a**$^+$ClO$_4^-$ (93%) of yellow needles.

$\delta(^{31}P)$ (acetone-d^6) = 11.8d, 8.3t (J_{PP} = 5 Hz)

C$_{38}$H$_{81}$Cl$_2$NiO$_4$P$_3$ (824.5); Calc./found: C, 55.35/55.49; H, 9.90/9.95%.

- A solution of AgSbF$_6$ (0.115 g, 0.33 mmol) in EtOH was added slowly to a solution of 250 mg of **4a**$^+$Cl$^-$ (0.33 mmol) in 8 ml EtOH. The white precipitate of AgCl was separated by filtration, and the orange coloured solution evaporated in vacuo. The remaining yellow powder was recrystallized from EtOH at −30°C. Yield 310 mg (98%) **4a**$^+$SbF$_6^-$.

$\delta(^{31}P)$ (acetone-d^6) = 11.9d, 8.2t (J_{PP} = 6 Hz)

C$_{38}$H$_{81}$ClF$_6$NiP$_3$Sb (960.8): Calc./found: C, 47.50/47.56; H, 8.50/8.46%.

4.8. Synthesis of 'Ni(PBu$_3$)$_2$(C$_6$Cl$_6$)' (6) and anion metathesis with NaClO$_4$

A solution of NiCl$_2$(PBu$_3$)$_2$ (12.37 g, 23.3 mmol) in 35 ml toluene was treated with Na dust (1.29 g, 56 mmol) under ethylene. After stirring for 30 h and centrifugation, the toluene solution was treated at −78°C with 6.5 ml standard ClC≡CCl solution (23 mmol).

The reaction mixture was kept for 15 min at this temperature and was then warmed to ambient temperature. After 20 min the solvent was removed in vacuo, and the remaining dark red oil examined by ^{31}P-NMR spectroscopy. The spectrum in acetone showed seven major components, which add up to 88% of the total integral intensity: From those signals, **3a** (δ = 9.3, 18%) and **4a**$^+$ (δ = 12.2d/10.7t; together 5%) could be identified and PBu$_3$O (δ = 46.2, br, 12%). There are also two AX spin systems (δ = 41.0d/ − 8.4d; together 24% and δ = 38.9d/ − 0.9d, together 6%) and two singlets at δ = 3.2 (16%) and δ = 4.2 (7%).

The oil was purified by chromatography on silica gel. Hexane/ether (1:1) eluted all of the PBu$_3$O and some of the minor components of the mixture. Ether alone eluted a red fraction, which contained, according to the ^{31}P-NMR spectrum, only one component. Evaporation of the solvent resulted in 0.72 g of a faint red powder, **6** (13%). C$_{30}$H$_{54}$Cl$_6$NiP$_2$ (748.0): Calc./found: C, 48.16/47.76; H, 7.28/7.20%. FAB-MS: 748 (^{12}C$_{30}$H$_{54}^{35}$Cl$_4^{37}$Cl$_2^{31}$P$_2^{58}$Ni, M$^+$), 711 (M$^+$-Cl).

A solution of **6** in acetone was treated with an excess of NaClO$_4$·H$_2$O with stirring for 1 h. Slow addition of water precipitated a pink powder, which was isolated and washed several times with water. Recrystallization from acetone/ether (2:5) at −30°C resulted in analytically pure **5a**$^+$ClO$_4^-$. C$_{30}$H$_{54}$Cl$_6$O$_4$P$_2$Ni (802.1): Calc./found: C, 44.92/44.55; H, 6.79/6.75%.

4.9. Synthesis of [Ni(C≡CPBu$_3$)$_2$(PBu$_3$)$_2$]$^+$(SbF$_6^-$]$_2$ (5)

A solution of **4a**$^+$Cl$^-$ (0.321 g, 0.42 mmol) in 4 ml EtOH was treated with an excess of AgSbF$_6$. After stirring for 5 min, the white precipitate of AgCl was removed by filtration. Addition of water precipitated a brownish powder which was isolated and washed several times with water. After drying in vacuo, the product was recrystallized from a small amount of MeOH at −30°C, which yielded 147 mg of **5** (51%) in the form of thin yellow needles. Crystals suitable for X-ray structure determination were obtained from a saturated EtOH solution at −30°C. C$_{52}$H$_{108}$F$_{12}$NiP$_4$Sb$_2$ (1387.0): Calc./found: C, 45.02/44.68; H, 7.85/7.62%.

4.10. Reaction of 6 with AgSbF$_6$ or CO: Formation of [Bu$_3$P(C$_6$HCl$_4$)]$^+$X$^-$ (8$^+$: X = SbF$_6$, Cl)

- An acetone solution of **6** (0.091 g, 0.122 mmol) was treated with an acetone solution of AgSbF$_6$ (0.045 g, 0.123 mmol), which resulted in the immediate formation of a white precipitate. Stirring was continued for a couple of minutes, before the suspension was filtered and the filtrate brought to dryness in vacuo. The remaining red oil was examined by ^{31}P-NMR spectroscopy. The spectrum of an acetone solution shows four components: **6** (δ = 41.1 br/ − 8.2 br; 10%), **7**$^+$SbF$_6^-$ (δ = 38.0s/ − 0.5s; 20%), Ag(PBu$_3$)$_x$(SbF$_6$) (δ = − 2.5 br, 30%) and **8**$^+$SbF$_6^-$ (δ = 38.9; 40%). The

oil was recrystallized from CH_2Cl_2/Et_2O (1:1) at r.t., which gave 61 mg of $\mathbf{8}^+SbF_6^-$ (77%) as an off-white powder. Cooling of the mother liquor to $-30°C$, gave ca. 8 mg of white crystals, which were identified by X-ray diffraction.

- A toluene solution of **6** was degassed in vacuo and then stirred for 5 h in a CO atmosphere. Evaporation of the solvent resulted in an off-white oil, which contained, according to its ^{31}P-NMR spectrum, only $\mathbf{8}^+Cl^-$ besides PBu_3O.

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers 117254 (compound **3c**) and 117255 (**5**).

Acknowledgements

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