results. The absolute differences between the theoretical harmonic frequency shifts and the anharmonic experimental shifts have been reduced to the 0.2–5.0 cm^{-1} range. That *all* of the frequency shifts come into better agreement with experiment as the theoretical model becomes more complete is almost as strong a statement about the $^1A_1$ state (Figure 3B) being the species observed by LFW as is the now overall good absolute agreement.

More convincing evidence that the spectra observed by LFW belongs to the $^1A_1$ state of Figure 3B is provided in Table IV, where we see that, at the CISD/DZP level of theory, the C–O stretching frequency, ω_7, in Si(CO)$_2$ is predicted to be 29 cm^{-1} *higher* than that in SiCO, in perfect agreement with experiment and in exact opposition to the SCF predictions.

Conclusion

Since it is so high-lying and does not correspond to a minimum on the potential energy surface, it seems clear that the linear centrosymmetric $^1\Sigma_g^+$ state of Si(CO)$_2$ is *not* the structure observed by Lembke, Ferrante, and Weltner[1] in their important matrix isolation studies. On the other hand, the agreement between the CISD theoretical predictions of the isotopic C–O frequency shifts and the experimentally observed values, coupled with the agreement between the theoretical and experimental C–O frequency differences between the SiCO and Si(CO)$_2$ molecules, provides strong evidence that the matrix IR spectra of LFW belongs to the $^1A_1$ state of C_{2v} symmetry in Figure 3B.

One important consequence of the proposed reduction in symmetry of the nuclear framework from $D_{\infty h}$ to C_{2v} is that the totally symmetric C–O stretching vibration, ω_1, is now IR active. At the CISD level of theory this mode is predicted to occur 115 cm^{-1} above the experimentally observed frequency ω_7, with about one-third the IR intensity. Predictions for the isotopic shifts corresponding to the mass combinations in Table III for this mode are 50.9, 20.4, 50.3, and 20.0 cm^{-1}, respectively. We hope these predictions will soon be verified in the laboratory. To aid the experimentalist, SCF and CISD force constants for structure B of Figure 3 are given in Table VI for the symmetry coordinates defined in Table V.

Finally, even though it seems likely that the experimentally observed spectra belong to the $^1A_1$ isomer in Figure 3B, there may well be lower lying isomers of SiC$_2$O$_2$. One intriguing possibility is a five-membered Si—O—C=C—O ring with 6π electrons. We leave these for possible future studies.

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Mono- and Bis(ethyne)nickel(0) Complexes

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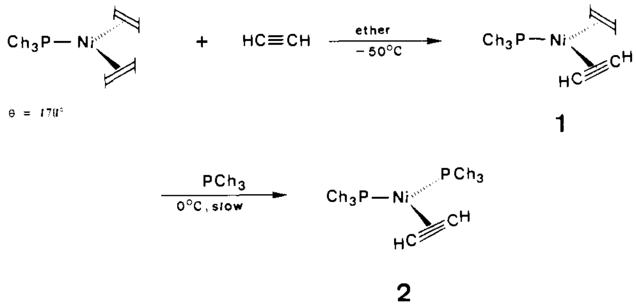
Abstract: Various (ligand)nickel(0)–ethene complexes react with ethyne in ether or pentane at low temperature to afford crystalline compounds of types $(R_3P)_2Ni(C_2H_2)$, $\{(RO)_3P\}_2Ni(C_2H_2)$, $(^tBuNC)_2Ni(C_2H_2)$, $(R_3P)Ni(C_2H_2)(C_2H_4)$, $\{(R_3P)Ni(C_2H_4)\}_2(\mu\text{-}C_2H_2)$, $\{(R_3P)Ni(C_2H_2)\}_2(\mu\text{-}C_2H_2)$, and $(R_3P)Ni(C_2H_2)_2$ (R = Me, Et, ^{i}Pr, Ch, Ph). The chemical and spectroscopic properties of the new complexes are reported.

Several catalytic processes are known involving nickel and ethyne, including the Reppe carbonylation of ethyne to acrylic acid,[1a] the cyclooligomerization of ethyne, which forms cyclooctatetraene (cot),[2a] higher oligomers,[2b] and benzene and styrene,[2c] the dimerization of ethene by an AlEt$_3$/nickel(0) catalyst activated and modified by ethyne,[3] and cooligomerization reactions of butadiene and ethyne yielding various products.[4] Nevertheless, especially the mechanism of the impressive ethyne tetramerization reaction to afford cot is still in question despite continued efforts toward its elucidation.[5]

Scheme I



The first step of any catalytic reaction between nickel and ethyne should involve the coordination of an ethyne molecule to the nickel atom. Complexes of nickel with ethyne are known for oxidation states II, I, and 0. When nickel salts are dissolved in liquid ethyne at 25 °C under pressure, they form labile adducts $(C_2H_2)_nNiX_2$ (n = 1–3).[6a] Complexes $(bpy)Ni(^iC_4H_9)_2(C_2H_2)$ and $(Ph_3P)_2Ni(^iC_4H_9)_2(C_2H_2)$ are reported to result from the reaction of Ni(acac)$_2$ with Al(^{i}C$_4$H$_9$)$_3$ in the presence of the ligand molecules at −78 °C.[6b] From the reaction of Cp$_2$Ni with ethyne at 70 °C under pressure the dinuclear compound $(CpNi)_2(\mu\text{-}C_2H_2)$

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is obtained, the crystal structure of which has been determined.[6c] Homoleptic complexes $Ni(C_2H_2)_n$ (n = 1, 2) may be trapped by matrix isolation technique and are stable only below −123 °C.[6d] For nickel complexes of other alkynes see ref. 7.

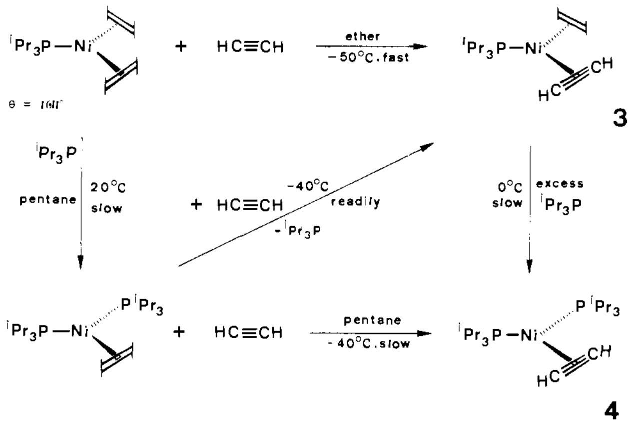
We have already described the synthesis and properties of bis(phosphane)nickel(0)–ethyne complexes[8-11] and communicated briefly on mono(phosphane)nickel(0)–ethyne complexes.[11,12] The present report expands our former work on bis(ligand)nickel(0)–ethyne complexes and provides detailed information on various types of mono(phosphane)nickel(0)–mono(ethyne) and -bis(ethyne) complexes.

Results

The coordination of an ethyne molecule to nickel(0) may be stabilized by coligands like phosphanes, phosphites, and *tert*-butyl isocyanide but not by 2,2-bipyridine (bpy) or *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (tmeda). (Phosphane)- and (phosphite)nickel(0)–ethyne complexes are best obtained upon reaction of the corresponding ethene complexes with ethyne in homogeneous solution (ether, pentane) at low temperatures (−78, 0 °C). For various phosphanes different types of complexes are formed, while for the phosphites studied so far and ^tBuNC, only bis(ligand)-nickel(0)–mono(ethyne) complexes have been obtained. In the following, the compounds with monodentate tertiary phosphanes PR_3 (R = alkyl, phenyl) as ligands to nickel(0) are presented in order of the phosphanes with decreasing steric requirements as described by the ligand cone angle θ.[13] Thereafter, (ethyne)-nickel(0) complexes with phosphites $P(OR)_3$ (R = methyl, phenyl, *o*-tolyl) and ^tBuNC as coligands will be reported.

(Cy_3P)$Ni(C_2H_4)(C_2H_2)$ (1) and (Cy_3P)$_2Ni(C_2H_2)$ (2) (Scheme I). The sterically most demanding monodentate phosphane used in this study is tricyclohexylphosphane (θ = 170°). It is already known that $(Cy_3P)Ni(C_2H_4)_2$[14] reacts with diphenylacetylene at −60/−45 °C to yield the mixed ethene–alkyne complex $(Cy_3P)Ni(C_2H_4)(C_2Ph_2)$.[15] Similarly, upon addition of ethyne to an ethereal solution of $(Cy_3P)Ni(C_2H_4)_2$ at −78/−50 °C, one ethene ligand is displaced by an ethyne molecule and the mixed ethene/ethyne complex **1** separates from the light yellow solution as small yellow crystals in 80% yield. A competition experiment showed that the ethene ligand is displaced by ethyne more readily than by phosphanes. Solid $(Cy_3P)Ni(C_2H_4)_2$ suspended in ether shows no reaction with ethyne at −78 °C. However, **1** is also obtained when the yellow crystalline product[8] of the reaction of tris(ethene)nickel(0)[16] and ethyne in ether is treated with PCy_3 below −100 °C. **1** is spectroscopically characterized by IR (1682 cm^{-1} (C_2H_2); 1497, 1225 cm^{-1} (C_2H_4)) and NMR spectra. The latter (^1H, 400 MHz; ^{13}C, 75.5 MHz) indicate that bonding of the ethyne ligand (δ(H) 7.00, 6.33; δ(C) 110.4, 104.8; J(CH) = 226, 223 Hz) is rigid at −10 °C, while the ethene ligand (δ(H) 2.58; δ(C) 52.0; J(CH) = 158 Hz) rotates around the bonding axis to nickel even at −100 °C. Solid **1** is stable up to 0 °C; it dissolves well in ether at −20 °C and recrystallizes upon cooling. From the reaction of **1** with cyclooctatetraene (cot) 90% of the ethene can be recovered but no ethyne. Both ethene (95%) and ethyne (82%) are liberated upon reaction of **1** with excess $P(OPh)_3$. **1** reacts with 3 equiv of carbon monoxide at −78 °C to yield $(Cy_3P)Ni(CO)_3$. Between **1** and butadiene, styrene, ethyl vinyl ether, acrylonitrile, vinyl chloride, or 2-butyne, no reaction was observed at −30 °C; the reaction products of **1** with diphenylacetylene (violet precipitate) and maleic anhydride (brown precipitate) have not been identified.

Scheme II



Reaction of **1** with phosphanes leads to displacement of the ethene ligand. With PMe_3 or $^1/_2$ equiv of bidentate bis(dimethylphosphino)ethane (dmpe) **1** reacts readily at −30 °C to yield the mixed phosphane complexes $(Cy_3P)(Me_3P)Ni(C_2H_2)$ (**2a**, 56%, light yellow crystals) and (dmpe){$(Cy_3P)Ni(C_2H_2)$}$_2$ (**2b**, 83%, large brown-yellow crystals). The reaction of **1** with another 1 equiv of Cy_3P proceeds slowly at 0 °C to give a clear deep brown solution from which light brown needles (70%) of the bis(phosphane) complex **2** are obtained. **2** also forms from $(Cy_3P)_2Ni$-(η^2-cdt), obtained as a light red ethereal solution from Ni(cdt) and 2 equiv of PCy_3.[17] With ethyne the reaction mixture becomes cloudy already at −78 °C, and at −30 °C red flocks of polyacetylene precipitate. Upon warming to 20 °C the color turns to violet, and further dark material (nickel, polyacetylene) precipitates. After filtration a clear red-brownish solution results from which **2**,[12] by other workers not obtained pure,[18] crystallizes overnight at 0 °C in about 40% yield. Stirring a yellow suspension of $(Cy_3P)_2Ni(C_2H_4)$[19] in ether with ethyne at −20 °C for 24 h also affords a dark violet reaction mixture under partial decomposition. However, among byproducts the precipitate contains only 60% of **2** and still unconverted educt ethene complex. **2** can be kept at 20 °C for storage. The compound solves poorly in THF and is rather insoluble in ether. From the reaction of **2** with excess $P(OPh)_3$ about 70% of the ethyne is recovered. IR and NMR data of the ethyne ligand in **2** (1627 cm^{-1}; δ(H) 6.41; δ(C) 121.1; J(CH) = 201 Hz) are typical for $(R_3P)_2Ni(C_2H_2)$ complexes with R = alkyl.

($^iPr_3P$)$Ni(C_2H_4)(C_2H_2)$ (3) and ($^iPr_3P$)$_2Ni(C_2H_2)$ (4) (Scheme II). Reactions of stoichiometric amounts of tris(ethene)nickel(0) and triisopropylphosphane (θ = 160°) in pentane at 0–20 °C afford the ethene complexes $(^iPr_3P)Ni(C_2H_4)_2$ and $(^iPr_3P)_2Ni(C_2H_4)$ (60%, large yellow plates). The compounds are very soluble in ether and pentane above −30 °C; below this temperature especially the monophosphane complex crystallizes very easily. From the reaction of $(^iPr_3P)Ni(C_2H_4)_2$ with 1 equiv of PMe_3 a mixture of $(^iPr_3P)_2Ni(C_2H_4)$ and $(Me_3P)_2Ni(C_2H_4)$ is obtained instead of the mixed phosphane complex. In $(^iPr_3P)_2Ni(C_2H_4)$ the ethene ligand cannot be displaced by excess phosphane.

When ethyne is added to the yellow solution of $(^iPr_3P)Ni(C_2H_4)_2$ in pentane at −50 °C, the color changes to light red and some polyacetylene flocks out. Cooling the filtrated solution

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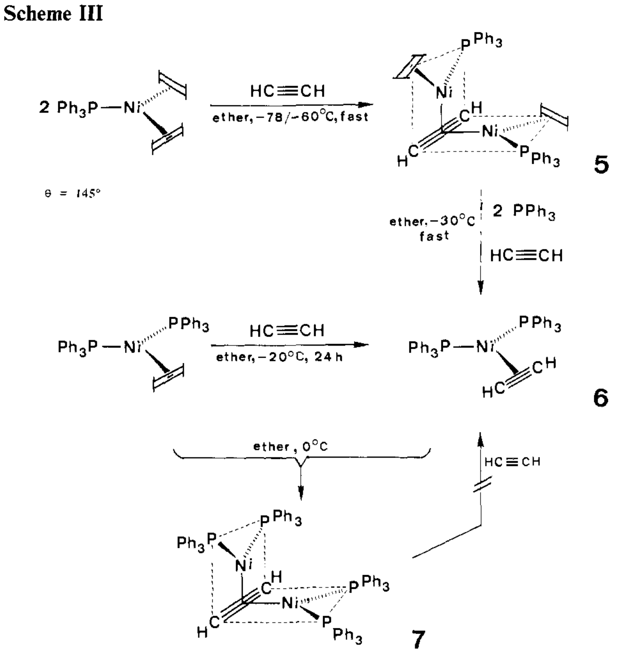
Scheme III



affords fine light yellow crystals of **3** in 70% yield. **3** dissolves well in pentane and decomposes at 0 °C. The reaction of **3** with excess $P(OPh)_3$ leads to recovery of the bound ethene (82%) and ethyne (38%). IR and NMR resonances of the ethyne (1682 cm^{-1}; δ(H) 7.00, 6.35; δ(C) 110.5, 104.9; J(CH) = 226, 221 Hz) and ethene ligands (1495, 1227 cm^{-1}; δ(H) 2.67; δ(C) 51.9; J(CH) = 158 Hz) in **3** are almost identical with those observed for **1**. **3** neither reacts further with ethyne nor with $({}^{i}Pr_3P)Ni(C_2H_4)_2$ at −40 °C (cf. below).

Upon addition of ethyne to the yellow pentane solution of $({}^{i}Pr_3P)_2Ni(C_2H_4)$ the color changes to deep red and then dark violet within a few minutes at −40/−30 °C. Moreover, brown polyacetylene precipitates after some time. Following the reaction by ${}^{31}P$ NMR shows that the conversion of the ethene educt complex into **4** is slow and is accompanied by the formation of **3** and free phosphane as byproducts. Obviously, one of the phosphane ligands in $({}^{i}Pr_3P)_2Ni(C_2H_4)$ is displaced by ethyne more readily than is the ethene ligand. The nature of the violet byproduct has not been clarified (possibly $({}^{i}Pr_3P)_3Ni$).

Pure **4** is obtained upon reaction of **3** with excess triisopropylphosphane at 20 °C. When ones starts from a pentane solution of tris(ethene)nickel(0), triisopropylphosphane, and ethyne, first **3** and then yellow-brownish crystals of **4** are formed in 65% yield. The reverse reaction, i.e,, the phosphane displacement in **4** by ethene to form **3**, is not observed at −30/0 °C. **3** reacts with 1 equiv of PMe_3 in pentane at −30 °C to afford the mixed phosphane complex $({}^{i}Pr_3P)(Me_3P)Ni(C_2H_2)$ (**4a**, yellow cubes, 72%). In the mass spectrometer **4** fragmentates with loss of ethyne to deliver $({}^{i}Pr_3P)_2Ni^+$ as largest mass observed, whereas for **4a** the molecular peak (320, 5%) is obtained.

Solid **4** is stable at 20 °C. It is more soluble in cold (−50 °C) pentane, ether, and THF than the corresponding ethene complex or **3**. The IR and NMR data of the ethyne ligand in **4** (1622 cm^{-1}; δ(H) 6,55; δ(C) 121.1; J(CH) = 201 Hz) are similar to those of the Ch_3P derivative **2**. **4** slowly catalyzes the conversion of ethyne to pure benzene at 20 °C (5 cycles in 20 h). **4** does not react with $Ni(C_2H_4)_3$ in pentane at 0 °C to afford **3** and $({}^{i}Pr_3P)Ni(C_2H_4)_2$.

$\{(Ph_3P)Ni(C_2H_4)\}_2(\mu\text{-}C_2H_2)\cdot Et_2O$ (5), $(Ph_3P)_2Ni(C_2H_2)$ (6), and $\{(Ph_3P)_2Ni\}_2(\mu\text{-}C_2H_2)$ (7) (Scheme III). Wilke and Herrmann prepared the first alkyne complexes of nickel(0) by reaction of $(Ph_3P)_2Ni(C_2H_4)$[19,20] with 2-butyne and diphenylacetylene to yield $(Ph_3P)_2Ni(C_2Me_2)$ and $(Ph_3P)_2Ni(C_2Ph_2)$.[20] Early attempts to obtain the corresponding ethyne complex failed,[21] although $(Ph_3P)_2Pt(C_2H_2)$ has been known for a long time.[22] As can be shown, however, stirring an ethereal suspension of $(Ph_3P)_2Ni(C_2H_4)$ with ethyne at −20 °C for 24 h leads to **6** as a yellow precipitate in quantitative yield. Well-formed crystals of **6** may be obtained by the stepwise procedure described below. The reaction of $(Ph_3P)Ni(C_2H_4)_2$[14,15] with disubstituted alkynes at −60/−45 °C is known to afford complexes like $(Ph_3P)Ni(C_2H_4)(C_2Me_2)$ and $(Ph_3P)Ni(C_2H_4)(C_2Ph_2)$.[15] In regard to its ligand cone angle θ = 145°, triphenylphosphane can be considered to be a phosphane ligand of medium size.

A suspension of $(Ph_3P)Ni(C_2H_4)_2$ in ether dissolves with $^1/_2$ mol equiv of ethyne at −50 °C to afford, upon cooling to −78 °C, the yellow microcrystalline precipitate of **5** (δ(P) 38.7), which decomposes above −20 °C.[9] The ${}^{1}H$ and ${}^{13}C$ NMR spectra of the dinuclear complex indicate a symmetrical coordination mode with an ethyne ligand (δ(H) 5.63; δ(C) 85.5; J(CH) = 210 Hz) bridging the nickel(0) centers and both phosphane and ethene ligands coordinated in a quasi-trans fashion to each other with respect to the Ni–Ni axis. At −78 °C $(Ph_3P)Ni(C_2H_4)_2$ suspended in ether shows no reaction with ethyne. From solutions obtained with an excess of ethyne at −50 °C, a mixture of ethyne complexes is obtained, which have not been separated from each other, Besides **5**, the compounds are presumed to have the compositions $\{(Ph_3P)Ni(C_2H_4)\}\{(Ph_3P)Ni(C_2H_2)\}(\mu\text{-}C_2H_2)$ (**5a**; δ(P) 43.8 (d), 40.8 (d); J(PP) = 7.6 Hz), $(Ph_3P)Ni(C_2H_4)(C_2H_2)$ (**5b**; δ(P) 44.5), $\{(Ph_3P)Ni(C_2H_2)\}_2(\mu\text{-}C_2H_2)$ (**5c**; δ(P) 45.3), and $(Ph_3P)Ni(C_2H_2)_2$ (**5d**; δ(P) 48.2).

Upon addition of 1 equiv of triphenylphosphane to the mixture of the products **5** and **5a–d** in the presence of ethyne at −78 °C and warming to −30 °C, yellow needles of the bis(phosphane)nickel(0) complex **6** (δ(P) 39.0) separate. Solid **6** is stable in air and decomposes only at 160 °C. The X-ray structure revealed a trigonal-planar coordination of the nickel atom by the PPh_3 ligands and the ethyne molecule. The Ni–C bonds both lie below the P–P–Ni plane (angle to plane about 5.2°); the ethyne H atoms even lie below the Ni–C–C plane and are turned away from the metal atom (H–C–C 148 (±2)°). The C–C distance of 1.239 (4) Å in the ethyne ligand is relatively short (cf. $({}^{i}Pr_2PC_2H_4P{}^{i}Pr_2)Ni(C_2H_2)$; 1.287 (7) Å.[9,11b] In solution, **6** slowly decomposes above 0 °C. **6** catalyzes the formation of benzene from ethyne. IR and NMR data (C_2H_2: 1629 cm^{-1}; δ(H) 6.41; δ(C) 122.1; ${}^{1}J$(CH) = 212 Hz) reflect the lower basicity of triphenylphosphane as compared to trialkylphosphanes. With ethyne-d_2 the deuterated derivative $(Ph_3P)_2Ni(C_2D_2)$ (**6a**) has been obtained, showing an IR absorption band for the C_2D_2 ligand at 1529 cm^{-1}. **6** does not reconvert with $Ni(C_2H_4)_3$ to yield **5**.

6 reacts with $(Ph_3P)_2Ni(C_2H_4)$ in THF solution at 0 °C to yield an orange precipitate **7** (δ(P) 23.4; 70%), stable at 20 °C, insoluble in THF, and only very weakly soluble in toluene. **7** is also obtained by addition of 2 equiv of PPh_3 to **5**. In the dinuclear complex **7** an ethyne molecule is bridging two bis(phosphane)nickel(0) units. No ethyne is evolved from **7** upon reaction with excess triphenyl phosphite. **7** is not converted by ethyne to give 2 equiv of mononuclear **6**. In the IR spectrum of **7** an absorption band, attributable to the C–C vibration, appears at 1368 cm^{-1}. For $\{(Ph_3P)_2Ni\}_2(\mu\text{-}C_2D_2)$ (**7a**) this band is shifted to 1316 cm^{-1}.

$(Et_3P)Ni(C_2H_4)(C_2H_2)$ (8), $\{(Et_3P)Ni(C_2H_4)\}_2(\mu\text{-}C_2H_2)$ (9), $(Et_3P)Ni(C_2H_2)_2$ (10), $(Et_3P)_2Ni(C_2H_2)$ (11), and $\{(Et_3P)_2Ni\}_2(\mu\text{-}C_2H_2)$ (12) (Scheme IV). Reaction of tris(ethene)nickel(0) with 1 and 2 equiv of the rather small triethylphosphane (θ = 132°) in pentane at 0 °C yields $(Et_3P)Ni(C_2H_4)_2$ or $(Et_3P)_2Ni(C_2H_4)$;[20] the latter has been known for a long time. Both compounds are very soluble in pentane down to −100 °C and are best reacted in situ.

$(Et_3P)Ni(C_2H_4)_2$ reacts with ethyne in pentane at −100 °C with rapid displacement of one ethene ligand to yield **8** (65%), which forms light yellow crystals decomposing above −78 °C. The NMR

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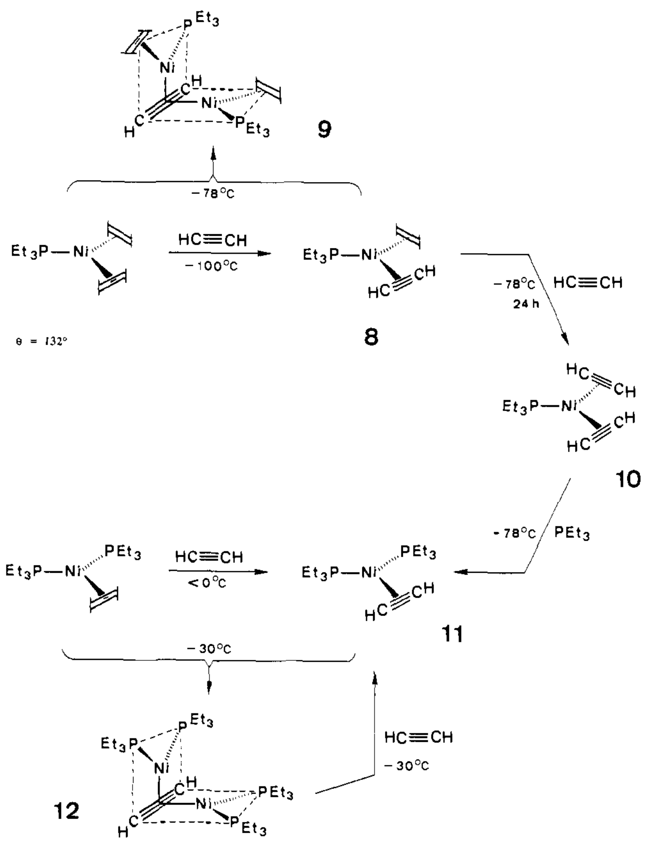
Scheme IV



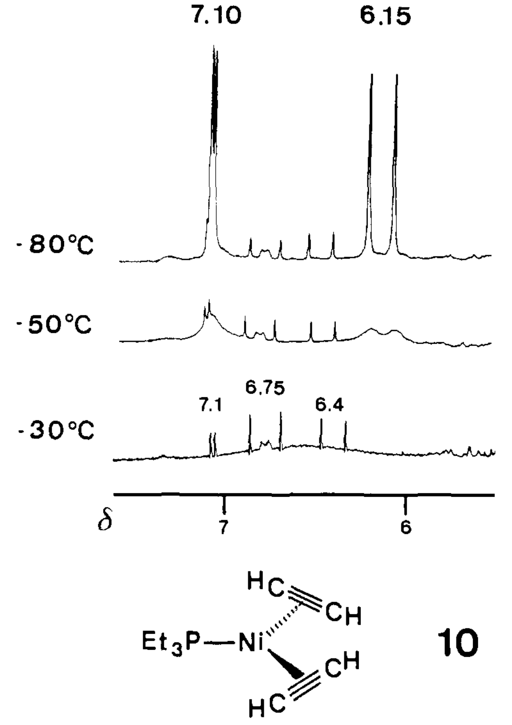
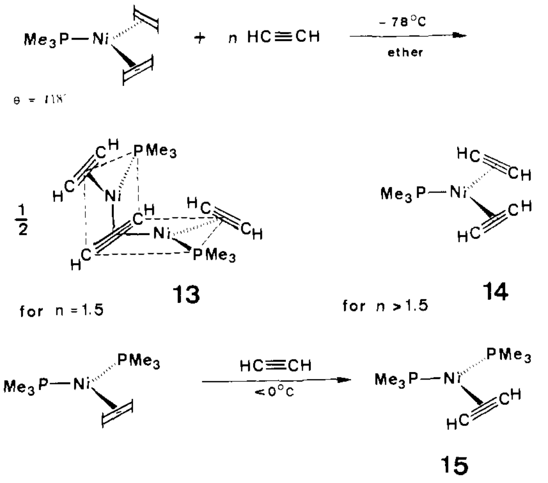


Figure 1. 200-MHz ^1H NMR resonances of the ethyne protons in $(Et_3P)Ni(C_2H_2)_2$ (**10**) between −80 and −30 °C. Purity of the sample about 85%; other components **11** (δ(H) 6.75) and **8** (δ(H) 7.1, 6.4).

Scheme V



data of **8** correspond to those of the cyclohexyl and isopropyl derivatives **1** and **3**. Reaction of **8** with the educt ethene complex $(Et_3P)Ni(C_2H_4)_2$ in pentane at a temperature as low as −78 °C affords the dinuclear complex **9** with bridging ethyne, the NMR data of which (δ(H) 5.67; δ(C) 79.6; J(CH) = 209 Hz) are similar to those of the PPh_3 derivative **5**. At −30 °C the ethene ligands of **9** deliver two signals for the diastereotopic protons (δ(H) 2.42, 2.30) and one for the carbon atoms (δ(C) 50.2) due to rotation of the ligands around their bonding axes to nickel. At −100 °C the carbon ethene signal collapses, and at −115 °C two carbon resonances (δ(C) 51.5, 47.5) are observed, indicating rigidly bound ethene ligands (as compared to the NMR time scale). Prolonged reaction of $(Et_3P)Ni(C_2H_4)_2$ with ethyne at −78 °C (24 h) causes, via **8**, displacement of also the second ethene ligand to yield the bis(ethyne)nickel(0) complex **10**. So far **10** has not been obtained pure but only as a mixture with 10–20% of **8** and minor amounts of **11**. No formation of $\{(Et_3P)Ni(C_2H_2)\}_2(\mu\text{-}C_2H_2)$ has been detected (cf. trimethylphosphane). The small yellow crystals of **10** decompose *at 0 °C* with *heavy detonation*. In the low-temperature (−80 °C) ^1H and ^{13}C NMR spectra the ethyne ligands give rise to two signals (δ(H) 7.10, δ(C) 95.8, ^1J(CH) = 227 Hz; δ(H) 6.15, δ(C) 104.4, ^1J(CH) = 232 Hz), indicating that the two ethyne carbon atoms lie in the trigonal-planar plane of the nickel atom with the methyne protons and carbon atoms being quasi-cis or -trans to phosphorus. With increasing temperature the signals coalesce due to rotation of the ligands around their bonding axis to nickel (Figure 1). From the coalescence temperature and the separation of the resonances in the NMR spectra (200 MHz) the activation energy of 46 kJ/mol has been estimated. This value lies about 10% above the barrier determined for the bis(ethene)nickel(0) complex $(Me_3P)Ni(C_2H_4)_2$.[23] No coupling of the ethyne ligands in **10** to form a nickelacyclopentadiene complex has been observed.

$(Et_3P)_2Ni(C_2H_4)$ reacts with ethyne in pentane instantly at −78 °C to form a light yellow solution, from which yellow cubes of **11** separate in 49% yield. **11** melts at about −15 °C and decomposes at 0 °C. **11** also forms from **8** or **10** with additional phosphane, displacing ethene (**8**) and ethyne (**10**). Reaction of **11** with $(Et_3P)_2Ni(C_2H_4)$ at −30 °C yields the dinuclear complex **12**, containing an ethyne ligand bridging two bis(phosphane)-nickel(0) moieties. Typically for complexes of this kind, the ^1H and ^{13}C NMR resonances of the μ-ethyne ligand (δ(H) 4.84; δ(C) 89.5; J(CH) = 187 Hz) are shifted high field as compared to mononuclear $(R_3P)_2Ni(C_2H_2)$ complexes, whereas the C–H coupling constant is further reduced. **12** may be reconverted to **11** by the addition of ethyne at −30 °C. All triethylphosphane complexes are markedly less stable than the ones of the larger phosphanes.

$\{(Me_3P)Ni(C_2H_2)\}_2(\mu\text{-}C_2H_2)$ (13), $(Me_3P)Ni(C_2H_2)_2$ (14), and $(Me_3P)_2Ni(C_2H_2)$ (15) (Scheme V). The syntheses of $(Me_3P)Ni(C_2H_4)_2$[23] and $(Me_3P)_2Ni(C_2H_4)$[8] have been described only recently. Both compounds dissolve extraordinary well in pentane or ether, even at −78 °C or below. With respect to the cone angle of $\theta = 118°$ trimethylphosphane is the sterically least demanding triorganylphosphane ligand to be discussed here.

$(Me_3P)Ni(C_2H_4)_2$ reacts with 1.5 equiv of ethyne in pentane at −78 °C to yield fine yellow crystals of **13**. In dinuclear **13** the

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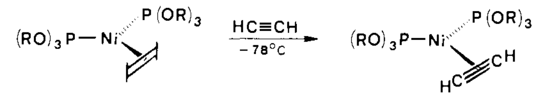
Scheme VI



16 R = Me
17 R = C6H5
18 R = C6H4-o-Me

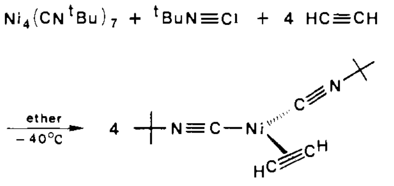
nickel atoms are coordinated to two ethyne ligands, one of the ethyne ligands of each nickel atom being bound in η^2 mode and one being shared by the nickel atoms as a bridging ligand. From ^{1}H and ^{13}C NMR spectra a symmetrical structure can be concluded, the two phosphorus ligands coordinated quasi-trans to each other. The η^2-HC≡CH ligands (δ(H) 6.88, δ(C) 101.1, ^1J(CH) = 224 Hz, cis to PMe$_3$; δ(H) 6.04, δ(C) 105.1, ^1J(CH) = 227 Hz, trans) and the bridging ethyne ligand (δ(H) 5.75, δ(C) 71.3, ^1J(CH) = 218 Hz) of **13** show distinctly different signals in the NMR spectra. If the reaction is carried out with excess of ethyne, the crystallization of **13** at −78 °C is followed by slow crystallization of yellow cubes of the bis(ethyne)nickel(0) complex **14**. ^{1}H and ^{13}C NMR data of **14** resemble those of the PEt$_3$ derivative **10**. Accordingly, the nickel atom is coordinated by the phosphane ligand and the ethyne ligands in a pseudo-trigonal-planar coordination geometry with the ethyne carbon atoms lying in the coordination plane. Both **13** and **14** are rather unstable, decomposing *at −60 °C* with *heavy detonation*, whereupon a 2:1 mixture of H_2 and CH_4 is formed. No complexes $(Me_3P)Ni(C_2H_4)(C_2H_2)$ or $\{(Me_3P)Ni(C_2H_4)\}_2(\mu\text{-}C_2H_2)$, analogous to the PEt$_3$ derivatives **8** and **9**, have been detected. Such species, if formed, obviously react easily further with ethyne under complete displacement of all ethene ligands.

$(Me_3P)_2Ni(C_2H_4)$ reacts with ethyne in pentane solution instantly at −78 °C, whereby the color of the reaction solution changes from yellow via orange-red back to yellow. At −100 °C yellow needles of **15** can be isolated in 71% yield.[8] **15** is extremely soluble even in cold pentane; the solid *explodes at 0 °C*. Unlike the synthesis of **7** and **12**, no $\{(Me_3P)_2Ni\}_2(\mu\text{-}C_2H_2)$ could be isolated upon reaction of equimolar amounts of $(Me_3P)_2Ni(C_2H_4)$ and **15** in pentane at −78 °C.

$\{(MeO)_3P\}_2Ni(C_2H_2)$ (16), $\{(PhO)_3P\}_2Ni(C_2H_2)$ (17), and $\{(Me\text{-}o\text{-}C_6H_4O)_3P\}_2Ni(C_2H_2)$ (18) (Scheme VI). Trialkyl and triaryl phosphites are sterically less demanding (P(OMe)$_3$, θ = 107°; P(OPh)$_3$, θ = 128°; P(OC$_6$H$_4$-o-Me)$_3$, θ = 141°) and less basic[24] ligands than the corresponding phosphanes. Ethene complexes $\{(RO)_3P\}_2Ni(C_2H_4)$ have been isolated only for triaryl phosphites substituted in the ortho position such as P(OC$_6$H$_4$-o-Ph)$_3$[20,25] and P(OC$_6$H$_4$-o-Me)$_3$.[20,26] Accordingly, for substituted alkynes, complexes of type $\{(R\text{-}o\text{-}C_6H_4O)_3P\}_2Ni(C_2R'_2)$[25,27] have been known for a long time, and the ethyne complexes $\{(Me\text{-}o\text{-}C_6H_4O)_3P\}_2Ni(C_2H_2)$ (**18**) and $\{(2\text{-Me-6-}^iPrC_6H_3O)_3P\}_2Ni(C_2H_2)$[18] have been described recently.

The yellow solutions of tris(ethene)nickel(0) and 2 equiv of the phosphites (MeO)$_3$P, (PhO)$_3$P, or (Me-o-C$_6$H$_4$O)$_3$P in pentane or ether react with ethyne at −78 °C to yield light yellow needles of **16** (51%; −25 °C dec), a light red precipitate of **17** (79%; 20 °C dec), or fine light yellow crystals of **18** (42%; 15 °C dec). In the IR spectra stretching vibrations ν(C≡C) of the bis(phosphite)nickel(0)–ethyne complexes have been observed at 1668 (**17**) and 1665 cm^{-1} (**18**), which are 40–50 cm^{-1} higher than found for bis(phosphane)nickel(0)–ethyne complexes. This indicates for phosphites a weaker back-bonding from nickel(0) to the ethyne ligand than with phosphanes as coligands. The same conclusion can be drawn from ^{13}C NMR data, which show less shielding of the ethyne carbon atoms (**16**, δ(C) 119.6, ^1J(CH) = 216 Hz; **17**, δ(C) 112.0, ^1J(CH) = 224 Hz) and a decreased reduction of the C–H coupling constant for the phosphite derivatives as compared to phosphane complexes. So far, neither bis(phosphite)nickel(0) complexes with bridging ethyne nor mono(phosphite)nickel(0)–ethyne complexes have been isolated.

Scheme VII



19

(^{t}BuN≡C)$_2$Ni(C$_2$H$_2$) (19) (Scheme VII). The reaction of bis(1,5-cyclooctadiene)nickel[28] with 2 equiv of *tert*-butyl isocyanide in pentane at 20 °C yields the cluster compound Ni$_4$(CN^{t}Bu)$_7$,[29] besides unreacted ^{t}BuNC. Upon addition of diphenylacetylene to this reaction mixture, $(Me_3CN{\equiv}C)_2Ni(C_2Ph_2)$[30] is formed. A 1:1:1 mixture of Ni(cod)$_2$, Me$_3$CN≡C, and C$_2$Ph$_2$ yields the cluster alkyne complex $(Me_3CN{\equiv}C)_4Ni_4(C_2Ph_2)_3$.[31]

Similarly, an equimolar mixture of $Ni_4(C{\equiv}NCMe_3)_7$ and Me$_3$CN≡C dissolved in ether reacts with ethyne at −40 °C to afford yellow-brownish needles of $(Me_3CN{\equiv}C)_2Ni(C_2H_2)$ (**19**; 62%). **19** is stable to about 0 °C. The NMR data of the ethyne ligand in **19** (δ(H) 6.57; δ(C) 115.2; J(CH) = 212 Hz) resemble those of the triphenylphosphane complex **6**, so that the electronic properties of the Me$_3$CN≡C ligand can be considered to be similar to those of PPh$_3$.

Discussion

Synthesis. The results presented above show that there are a large number of mono- and bis(ethyne) complexes of nickel(0) accessible with phosphanes as well as phosphites or *tert*-butyl isocyanide as coligands. For monodentate tertiary phosphanes R$_3$P (R = alkyl, phenyl) the product complexes are best formed by displacing the olefinic ligand of (alkene)nickel(0) complexes with ethyne at low temperature. The type of product complex formed and its thermal properties are mainly directed by both the stoichiometries employed and the steric requirements of the stabilizing ligands. In principle, all ethyne nickel(0) complexes found can be deduced to 6 basic types.

For mono(phosphane)bis(ethene)nickel(0) complexes $(R_3P)Ni(C_2H_4)_2$ with phosphanes with large cone angles (R = Ch, ^{i}Pr; $\theta \geq$ 160°) only one ethene ligand is displaced by ethyne under relatively mild conditions (−78 to 0 °C) to give the *mononuclear* mixed π-ligand mono(phosphane)(*ethene*)(*ethyne*)nickel(0) complexes *$(R_3P)Ni(C_2H_4)(C_2H_2)$* **1** and **3**, which are thermally stable to about 0 °C. Essentially the large size of the phosphane prevents the substitution of the remaining ethene ligand by a second ethyne molecule. Also, for ligands with large cone angles it appears that steric repulsion prevents the formation of dinuclear compounds by coupling two $(R_3P)Ni(C_2H_4)$ units via a bridging ethyne ligand.

For triphenylphosphane, a ligand of intermediate size (θ = 145°), the reaction of $(R_3P)Ni(C_2H_4)_2$ with excess ethyne at low temperature leads to a series of ethyne complexes, of which only the *dinuclear* mixed π-ligand mono(phosphane)(*ethene*)(*ethyne*)nickel(0) derivative *$\{(R_3P)Ni(C_2H_4)\}_2(\mu\text{-}C_2H_2)$* **5** could be isolated pure by adding the stoichiometric amount of ethyne. The preparations are complicated by decomposition temperatures of the product complexes as low as −40 °C. However, it seems that

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in principle both ethene ligands of the starting complex can be displaced by ethyne to form mono- and dinuclear mono- and bis(ethyne)nickel(0) complexes.

For smaller phosphane ligands (R = Et, Me; $\theta \leq 132^\circ$) the reaction of the $(R_3P)Ni(C_2H_4)_2$ starting complexes with ethyne may be stopped at the $(R_3P)Ni(C_2H_4)(C_2H_2)$ stage only for R = Et at −100 °C to give **8**. On isolation, **8** decomposes just above −78 °C. By interaction of **8** with another 1 equiv of educt complex, the dinuclear mixed π-ligand derivative **9** can by synthesized, showing increased thermal stability. In solution, the ethene ligand of the intermediate **8** is slowly displaced by excess ethyne at −78 °C to yield the corresponding *mononuclear* mono(phosphane)-*bis(ethyne)*nickel(0) complex $(R_3P)Ni(C_2H_2)_2$ **10**, stable to about 0 °C. For R = Me, the reaction of $(R_3P)Ni(C_2H_4)_2$ at −100 or −78 °C causes rapid displacement of all ethene ligands to yield the *dinuclear* mono(phosphane)*bis(ethyne)*nickel(0) derivative $\{(R_3P)Ni(C_2H_2)\}_2(\mu\text{-}C_2H_2)$ **13** as the first isolable product. With excess of ethyne the mononuclear bis(ethyne) complex **14** is also formed.

In short, the steric requirements in $(R_3P)Ni(C_2H_2)_2$ complexes appear to permit the coordination of two ethyne ligands to the nickel atom only if the monodentate triorganylphosphane ligand has a cone angle θ of less than 145°.

For the discussion of the ethyne bis(ligand)nickel(0) complexes, it is appropriate to examine first the influence of small phosphanes and phosphites with cone angles $\theta \leq 141^\circ$. In $(R_3P)_2Ni(C_2H_4)$ (R = Me, Et) and $\{(R'O)_3P\}_2Ni(C_2H_4)$ (R′ = Me, Ph, C_6H_4-*o*-Me) the ethene ligands are readily displaced even at −78 °C to form the corresponding *mononuclear* bis(phosphane)- and bis(phosphite)*mono(ethyne)*nickel(0) complexes $(R_3P)_2Ni(C_2H_2)$ **11** and **15** and $\{(R'O)_3P\}_2Ni(C_2H_2)$ **16–18**. These complexes of the smaller ligands decompose at 0 °C or not much above. **11** (R = Et) combines with the educt ethene complex at −30 °C to yield the *dinuclear* bis(phosphane)*mono(ethyne)*nickel(0) derivative $\{(R_3P)_2Ni\}_2(\mu\text{-}C_2H_2)$ **12**. A similar reaction probably occurs at −78 °C for R = Me, but it has not been possible to isolate the product. For the phosphite derivatives the dimerization reaction has not been tested so far.

The $(R_3P)_2Ni(C_2H_4)$ complex of medium-sized Ph_3P reacts only slowly with ethyne at −20 °C to afford the ethyne complex **6** as a precipitate. The $^iPr_3P$ and Ch_3P educt complexes no longer show simple alkene displacement reactions. For $(^iPr_3P)_2Ni(C_2H_4)$ the displacement of a phosphane ligand by ethyne has been shown to yield a mixture of **3** and **4**. Therefore, complexes $(R_3P)_2Ni(C_2H_2)$ of phosphanes with cone angles $\theta \geq 145^\circ$ are best prepared in a *stepwise procedure* by reacting $(R_3P)Ni(C_2H_4)_2$ complexes successively with ethyne and additional phosphane between −30 and 20 °C. The resulting well-crystallized product complexes are of surprisingly high thermal and chemical stability (e.g., toward air). Although the dinuclear derivative $\{(R_3P)_2Ni\}_2(\mu\text{-}C_2H_2)$ can still be prepared for R = Ph, the synthesis fails for the larger phosphanes with R = ^{i}Pr and Ch due to steric repulsion of the ligands.

Spectroscopic Properties. The exchange of an ethene ligand of a (phosphane)nickel(0) complex by ethyne is accompanied by a downfield shift of the ^{31}P NMR resonance [e.g., $(Et_3P)_2Ni(C_2H_4)$, δ(P) 18.9; $(Et_3P)_2Ni(C_2H_2)$ (**11**), δ(P) 24.7 (however, $\{(Et_3P)_2Ni\}_2(\mu\text{-}C_2H_2)$ (**12**), δ(P) 15.9) and $(Et_3P)Ni(C_2H_4)_2$, δ(P) 23.2; $(Et_3P)Ni(C_2H_4)(C_2H_2)$ (**8**), δ(P) 26.8; $(Et_3P)Ni(C_2H_2)_2$ (**10**), δ(P) 29.4]. This trend is consistent with a deshielding of phosphorus due to partial oxidation of the nickel atom.

The ^1H NMR resonances of the ethyne molecules are shifted downfield from δ(H) 2.4 (THF-d_8) for unbound ethyne to the range of about 7.2–5.5 for ethyne coordinated to one nickel center. The downfield shift reflects the decrease of bond order of the C–C triple bond with the hydrogen atoms becoming vinylic. Coordination of a second nickel atom to the ethyne π-orbital perpendicular to the one to which the first nickel atom is already bound causes an opposite shift to higher field of about 1–2 ppm [e.g., $(Et_3P)Ni(C_2H_4)(C_2H_2)$ (**8**), δ(H) 7.11, 6.48; $\{(Et_3P)Ni(C_2H_4)\}_2(\mu\text{-}C_2H_2)$ (**9**), δ(H) 5.67 and $(Et_3P)_2Ni(C_2H_2)$ (**11**), δ(H) 6.75; $\{(Et_3P)_2Ni\}_2(\mu\text{-}C_2H_2)$ (**12**), δ(H) 4.84]. The high-field shift can be rationalized by assuming that the C–C bond order is lowered from 2 to 1, shifting the resonances in the direction of signals expected for hydrocarbons. A similar, even more pronounced tendency of reverse chemical shifts can be made out for the ^{13}C NMR ethyne resonances. However, the ethyne coupling constants J(CH) show a steady decrease from J(CH) = 249 Hz of unbound ethyne through the values of the bis(phosphite)nickel(0) complexes **17** (224 Hz) and **16** (216 Hz), the bis(triphenylphosphane)- and bis(isocyanide)nickel(0) complexes **6** and **19** (both 212 Hz), the bis(trialkyl)phosphane complexes **2**, **4**, and **15**[8] (all 201 Hz) to complexes with bridging ethyne ligands as **12** (187 Hz). The declining carbon–hydrogen spin–spin coupling constant can be interpreted as reflecting a decreasing s character of the C–H bonds and a hybridization change of the carbon atom $sp \rightarrow sp^2 \rightarrow sp^3$. The higher the basicity of the donor ligands and the more metal atoms the ethyne molecule is bound to the stronger this hybridization change is.

Chemical Properties. Ethyne coordinated to nickel(0) in donor ligand stabilized complexes appears to be rather resistant to chemical conversions. The high thermal stability of the solid complexes with bulky phosphanes as well as their surprising stability toward air has already been pointed out. However, in solution the thermal stability of the complexes seems to be limited to about 20 °C for the most stable derivatives. Up to the decomposition temperature, reactions have not been observed with mild acids (CH_3OH, acetylacetone) or bases (butyllithium in ether, sodium bis(trimethylsilyl)amide in THF, sodium hydridoboronate and -aluminate complexes). Strong acids (HCl gas) oxidize nickel(0) to nickel(II) ($NiCl_2$). Hydrogenation of coordinated ethyne to an ethene ligand has not been achieved. The addition of boron hydrides to the ethyne ligand triple bond to form vinylboron complexes and the coupling of coordinated ethyne with CO_2 and C_2F_4 to form nickelacyclopentene derivatives are still under investigation. The nickel(0)-bound ethyne does not rearrange to a vinylidene ligand $Ni{=}C{=}CH_2$ or undergo oxidative addition of the ethyne C–H bond to nickel(0) to form an ethynyl(hydride)nickel(II) complex.[32]

Complexes with two ethyne ligands bound to one metal center are rather scarce.[33,34] For the presented mono- and dinuclear nickel(0) compounds with more than one ethyne ligand no indication was found for a coupling of the ethyne ligands to form nickelacyclopentadiene or related complexes, as has been observed for another system.[11a] This is especially remarkable for complexes of type $(R_3P)Ni(C_2H_2)_2$ (**10**, **14**) and $\{(Me_3P)Ni(C_2H_2)\}_2(\mu\text{-}C_2H_2)$ (**13**), which have two or even three ethyne ligands bound next to one another. Obviously, the mechanism of coupling of ethyne ligands is more subtle than one might suspect.

Experimental Section

The reaction conditions and spectroscopic instruments have been described elsewhere.[8] To exclude oxygen and moisture, all manipulations were carried out by an open-bench technique with Schlenk-type glassware under argon. Starting complexes were prepared according to cited procedures. Commercially available phosphanes (Alfa, Strem) were used without further purification; phosphites were degassed by distillation in vacuo. Microanalyses were performed by the Mikroanalytisches Labor Dornis und Kolbe, Mülheim a.d. Ruhr. ^1H NMR, 200 MHz, Bruker AM-200 (relative to internal TMS); ^{13}C NMR, 75.5 MHz, Bruker WM-300 (relative to internal TMS); ^{31}P NMR, 32.4 MHz, Bruker WP-80 (relative to external 85% aqueous H_3PO_4). *Warning!* The compounds exploding at 0 °C or below should only be handled with safety precautions (safety glasses, leather gloves) and in small quantities.

New (Ligand)nickel–Ethene Complexes. $(Et_3P)Ni(C_2H_4)_2$. A solution of $Ni(C_2H_4)_3$,[16] prepared from 1.165 g (5.0 mmol) of Ni(cdt)[28] in 20 mL of pentane and ethene at 0 °C, is added to 590 mg (5.0 mmol) of PEt_3, giving 5.0 mmol of $(Et_3P)Ni(C_2H_4)_2$. Insoluble impurities are removed by filtration. The complex does not crystallize from pentane solution at

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−78 °C. ^{31}P NMR (THF-d_8, −30 °C): δ 23.2.

$(^iPr_3P)Ni(C_2H_4)_2$. A pentane solution (30 mL) of 10.0 mmol of $Ni(C_2H_4)_3$ is prepared from 2.33 g (10.0 mmol of Ni, 5% cdt) of Ni(cdt) and ethene and is added to 1.60 g (10:0 mmol) of P^iPr_3 at 0 °C. After filtration to remove insoluble impurities, large yellow crystals are obtained at −78 °C. The mother liquor is separated by a capillary, and the compound is washed twice with cold pentane and dried in vacuo at −30 °C; yield 2.31 g (84%). The complex is very soluble in pentane and ether but less soluble in THF; it crystallizes from ether or pentane very well upon cooling. ^{1}H NMR (THF-d_8, −20 °C): δ 2.40 (C_2H_4), 2.35 (m, PCH), 1.17 (m, CH_3). ^{31}P NMR (THF-d_8, −20 °C): δ 50.4. Anal. Calcd for $C_{13}H_{29}NiP$ (275.1): C, 56.77; H, 10.63; Ni, 21.34; P, 11.26. Found: C, 56.49; H, 10.96; Ni, 21.28; P, 11.19.

$(^iPr_3P)_2Ni(C_2H_4)$. A pentane solution (25 mL) of 10.0 mmol of $Ni(C_2H_4)_3$, obtained from 2.33 g (10.0 mmol Ni, 5% cdt) of Ni(cdt) and ethene, is added to at least 3.20 g (20.0 mmol) of P^iPr_3 at 0 °C (50% phosphane excess recommended). After keeping the intense yellow reaction solution at 20 °C for 1 h, insoluble impurities are removed by filtration. Between −30 and −78 °C yellow plates crystallize, which after separation of the mother liquor by means of a capillary are washed twice with cold pentane and dried in vacuo at 20 °C; yield 2.69 g (66%); stable at 20 °C. Concentrating the mother liquor yields more product mixed with cdt. 400-MHz ^{1}H NMR (THF-d_8, 27 °C): δ 2.13 (m, 6 H, PCH), 1.58 (s, 4 H, C_2H_4), 1.22 (m, 36 H, CH_3). 32.4-MHz ^{31}P NMR (THF-d_8, −30 °C): δ 48.6. Anal. Calcd for $C_{20}H_{46}NiP_2$ (407.2): C, 58.99; H, 11.39; Ni, 14.42; P, 15.21. Found: C, 59.22; H, 11.09; Ni, 14.32; P, 15.21.

(Ligand)nickel(0)–Ethyne Complexes. $(Ch_3P)Ni(C_2H_4)(C_2H_2)$ (1). A total of 50 mL (6 mmol) of ethyne is added at −50 °C without stirring to an ethereal solution (40 mL) of 5.0 mmol of $(Ch_3P)Ni(C_2H_4)_2$,[14,15] prepared from 1.165 g (5.0 mmol Ni) of Ni(cdt), ethene, and 1.40 g (5.0 mmol) of PCh_3. The color of the yellow solution changes to light red, and at −78 °C in the course of 2 days small yellow crystals form. The mother liquor is removed by a capillary, the crystals are washed twice with cold ether and dried in vacuo at −30 °C: yield 1.62 g (82%); above 0 °C dec. IR (KBr): 1682 cm^{-1} (C_2H_2), 1497, 1225 cm^{-1} (C_2H_4). ^{1}H NMR (THF-d_8, 0 °C): δ 6.91 (d, J(PH) = 4.5 Hz), 6.23 (d, J(CH) = 22.4 Hz, C_2H_2), 2.65 (d, J(CH) = 1.5 Hz, C_2H_4), 2.3–1.2 (br, Ch). ^{13}C NMR (THF-d_8, 0 °C): δ 110.4 (m, ^1J(CH) = 226 Hz, ^3J(CH) = 24 Hz, J(PC) = 18.5 Hz), 104.8 (m, ^1J(CH) = 220 Hz, ^3J(CH) = 25 Hz, J(PC) = 12.5 Hz, C_2H_2), 52.1 (t, J(CH) = 158 Hz, C_2H_4), 36.0, 30.8, 28.6, 27.5 (Ch_3P). ^{31}P NMR (THF-d_8, 0 °C): δ 43.8. Anal. Calcd for $C_{22}H_{39}NiP$ (393.2): C, 67.20; H, 10.00; Ni, 14.93; P, 7.88. Found: C, 67.08; H, 9.86; Ni, 15.11; P, 7.88.

Reaction of 1 with cot: 1.05 g (2.67 mmol) of solid **1** reacted with excess cot to liberate 2.4 mmol of ethene (90%) but no ethyne.

Reaction of 1 with $P(OPh)_3$: 388.5 mg (0.99 mmol) of solid **1** reacted with excess $P(OPh)_3$ to yield 0.94 mmol of ethene (95%) and 0.81 mmol of ethyne (82%).

Reaction of 1 with CO: 833 mg (2.12 mmol) of **1** were suspended in 40 mL of ether at −78 °C. Upon stirring with CO (5.63 mmol, 2.66 CO/Ni) the color changed from yellow to light red and a colorless precipitate formed, which was recrystallized by warming. Yield 300 mg (0.71 mmol) of $(Ch_3P)Ni(CO)_3$ (33%).

$(Ch_3P)_2Ni(C_2H_2)$ (2). (a) An ethereal solution (60 mL) of 5.0 mmol $Ni(C_2H_4)_3$, made from 1.165 g (5.0 mmol Ni, 5% cdt) of Ni(cdt) and ethene, and of 2.80 g (10.0 mmol) of PCh_3 is exposed to about 150 mL (6 mmol) of ethyne at −70 °C. The red reaction mixture is kept at 0 °C overnight and filtrated. At −30 °C yellow-brownish needles are obtained, which, after separation of the mother liquor by capillary, are washed twice with cold ether and dried in vacuo at 20 °C; yield 2.26 g (70%).

(b) A solution of 1.165 g (5.0 mmol Ni, 5% cdt) of Ni(cdt) and 2.80 g (10.0 mmol) of PCh_3 in 50 mL of ether is kept at 20 °C for several hours to form the light red solution of $(Ch_3P)_2Ni(\eta^2\text{-cdt})$.[17] After addition of about 150 mL (6 mmol) of ethyne at −78 °C, the reaction solution is warmed to 20 °C for 1 h. The sludgy violet mixture is filtrated, and from the clear red-brownish solution, the product is obtained and isolated as described above; yield 1.48 g (46%). IR (KBr): 1627 cm^{-1} (C_2H_2). ^{1}H NMR (THF-d_8, 27 °C): δ 6.41 (m, C_2H_2), 2.1–1.2 (br, PCh_3). ^{13}C NMR (THF-d_8, −10 °C): δ 121.1 (m, ^1J(CH) = 201 Hz, C_2H_2), 36.9, 31.1, 28.9, 27.7 (PCh_3). ^{31}P NMR (THF-d_8, 38 °C): δ 44.3. Anal. Calcd for $C_{38}H_{68}NiP_2$ (645.6): C, 70.70; H, 10.62; Ni, 9.09; P, 9.60. Found: C, 70.46; H, 9.96; Ni, 8.98; P, 9.40.

Reaction of 2 with $P(OPh)_3$: 537 mg (0.83 mmol) of **2** reacted with excess $P(OPh)_3$ to yield 0.57 mmol of ethyne (69%).

$(Ch_3P)(Me_3P)Ni(C_2H_2)$ (2a). An ethereal solution (50 mL) of 5.0 mmol $(Ch_3P)Ni(C_2H_4)(C_2H_2)$ (**1**), made as described above, is combined with 380 mg (5.0 mmol) of PMe_3 in 10 mL of ether at −30 °C. The color of the reaction solution darkens, and some polyacetylene flocks out. After a short while light yellow crystals separate, which are kept at −78 °C overnight. The mother liquor is drained off through a capillary and the crystals are washed twice with cold pentane and dried in vacuo at −30 °C: yield 1.24 g (56%); stable at 20 °C. ^{1}H NMR (THF-d_8, −30 °C): δ 6.69 (m, 1 H), 6.56 (m, 1 H, C_2H_2), 2.4–1.1 (br, 33 H, PCh_3), 1.28 (d, J(PH) = 6 Hz, 9 H, PMe_3). ^{31}P NMR (THF-d_8, −40 °C): δ 48.6 (d), −13.2 (d), J(PP) = 23.2 Hz. Anal. Calcd for $C_{23}H_{44}NiP_2$ (441.3): C, 62.61; H, 10.05; Ni, 13.30; P, 14.04. Found: C, 62.16; H, 9.75; Ni, 13.61; P, 14.41.

Reaction of 2a with $P(OPh)_3$: Upon reaction of 1.00 g (2.27 mmol) of **2a** with excess $P(OPh)_3$, 1.68 mmol of ethyne (74%) were recovered.

(dmpe)$\{(Ch_3P)Ni(C_2H_2)\}_2$ (2b). Syntheses were as for **2a**, with addition of 375 mg (2.50 mmol) of dmpe, yielding large brown-yellow crystals from a light yellow solution, isolated as described: yield 1.83 g (83%). IR (KBr): 1618 cm^{-1} (C_2H_2). ^{1}H NMR (THF-d_8, −30 °C): δ 6.62 (m, 4 H, C_2H_2), 2.1–1.1 (br, 82 H, PCh_3, dmpe). ^{31}P NMR (THF-d_8, −30 °C): δ 48.4 (^2J(PP) = 23.0 Hz, PCh_3), −0.1 (^3J(PP) = 36.3 Hz, dmpe) AA′XX′. Anal. Calcd for $C_{46}H_{86}Ni_2P_4$ (880.5): C, 62.75; H, 9.84; Ni, 13.34; P, 14.07. Found: C, 62.83; H, 9.86; Ni, 13.28; P, 13.92.

Reaction of 2b with $P(OPh)_3$: Upon reaction of 2.11 g (2.40 mmol) of **2b** with excess $P(OPh)_3$, 3.71 mmol of ethyne (77%) were recovered.

$(^iPr_3P)Ni(C_2H_4)(C_2H_2)$ (3). The yellow solution of 1.37 g (5.0 mmol) of $(^iPr_3P)Ni(C_2H_4)_2$ in 20 mL of pentane is exposed to about 150 mL (6 mmol) of ethyne at −50 °C without stirring. Soon light yellow crystals separate. After complete crystallization at −78 °C the mother liquor is taken off by means of a capillary, and the crystals are washed twice with cold pentane and dried in vacuo at −30 °C: yield 950 mg (70%); above −20 °C dec; dissolves well in ether. IR (KBr): 1682 cm^{-1} (C_2H_2), 1495, 1227 cm^{-1} (C_2H_4). ^{1}H NMR (THF-d_8, −30 °C): δ 7.00 (d, J(PH) = 4.5 Hz), 6.35 (d, J(PH) = 22.6 Hz, C_2H_2), 2.67 (C_2H_4), 2.43 (m, PCH), 1.17 (m, CH_3). ^{13}C NMR (THF-d_8, −50 °C): δ 110.5 (J(PC) = 18.3 Hz, ^1J(CH) = 226 Hz, ^3J(CH) = 24 Hz), 104.9 (J(PC) = 12.7 Hz, ^1J(CH) = 221 Hz, ^3J(CH) = 25 Hz, C_2H_2), 51.9 (J(PC) = 1 Hz, J(CH) = 158 Hz, C_2H_4), 26.0 (PC), 20.1 (CH_3). ^{31}P NMR (THF-d_8, −30 °C): δ 54.6. Anal. Calcd for $C_{13}H_{27}NiP$ (273.0): C, 57.19; H, 9.97; Ni, 21.50; P, 11.34. Found: C, 57.26; H, 9.95; Ni, 21.41; P, 11.26.

Reaction of 3 with $P(OPh)_3$: Upon reaction of 593 mg (2.17 mmol) of **3** with excess $P(OPh)_3$, 1.79 mmol of ethene (82%) and 0.82 mmol of ethyne (38%) were recovered.

$(^iPr_3P)_2Ni(C_2H_2)$ (4). To a pentane solution (25 mL) of 5.0 mmol of $Ni(C_2H_4)_3$ (see above) and about 2.4 g (15 mmol) of P^iPr_3 are quickly added at −30 °C about 150 mL (6 mmol) of ethyne. The color of the reaction solution turns from yellow to red, and some violet material precipitates. After warming to 20 °C for 30 min the now deep violet mixture is filtered to result in an intense red-brown solution. At −78 °C yellow-brownish crystals separate, which are drained by means of a capillary, washed twice with cold pentane, and dried in vacuo at −30 °C: yield 1.32 g (65%); stable at 20 °C; good solubility in pentane. MS (70 eV, 56 °C): m/z (% rel intens) 378 ($M^+ - C_2H_2$, 100). IR (KBr): 1622 cm^{-1} (C_2H_2). ^{1}H NMR (THF-d_8, −50 °C): δ 6.55 (m, C_2H_2), 2.18 (m, PCH), 1.22 (m, CH_3). ^{13}C NMR (THF-d_8, −30 °C): δ 121.15 (^1J(CH) = 201 Hz, ^3J(CH) = 15 Hz, C_2H_2), 27.0 (PCH), 20.6 (CH_3). ^{31}P NMR (THF-d_8, −30 °C): δ 53.8. Anal. Calcd for $C_{20}H_{44}NiP_2$ (405.2): C, 59.28; H, 10.94; Ni, 14.49; P, 15.29. Found: C, 58.84; H, 11.40; Ni, 14.32; P, 15.36.

$(^iPr_3P)(Me_3P)Ni(C_2H_2)$ (4a). To a solution of 2.75 g (10.0 mmol) of $(^iPr_3P)Ni(C_2H_4)_2$ in 20 mL of pentane are added 760 mg (10.0 mmol) of PMe_3 and 270 mL (11 mmol) of ethyne at −30 °C to afford an intense yellow reaction solution. At −78 °C yellow cubes separate, which are isolated as described above: yield 2.31 g (72%); mp 0 °C; very soluble in pentane and other solvents. MS (70 eV, 10 °C): m/z (% rel intens) 320 (M^+, 5), 294 ($M^+ - C_2H_2$, 25), 76 (PMe_3^+, 100). ^{1}H NMR (THF-d_8, −30 °C): δ 6.72 (m, 1 H, J(PH) = 10.3, 25.4 Hz), 6.68 (m, 1 H, J(PH) = 11.6, 19.3 Hz, ^3J(HH) = 1.5 Hz, C_2H_2), 2.07 (m, 3 H, PCH), 1.28 (d, 9 H, J(PH) = 5.8 Hz, PMe_3), 1.19 (m, 18 H, J(PH) = 12.5 Hz, CCH_3). ^{31}P NMR (THF-d_8, −30 °C): δ 60.3 (d, P^iPr_3), −14.0 (d, PMe_3), J(PP) = 23.1 Hz. Anal. Calcd for $C_{14}H_{32}NiP_2$ (321.1): C, 52.37; H, 10.05; Ni, 18.29; P, 19.29. Found: C, 52.22; H, 10.14; Ni, 18.19; P, 19.36.

$\{(Ph_3P)Ni(C_2H_4)\}_2(\mu\text{-}C_2H_2)\cdot Et_2O$ (5). To a suspension of 1.885 g (5.0 mmol) of $(Ph_3P)Ni(C_2H_4)_2$ in 30 mL of ether is added at −78 °C ca. 75 mL (3 mmol) ethyne. The reaction mixture is warmed to −45 °C under stirring, whereupon for a short time a clear solution results, from which a yellow microcrystalline precipitate is obtained. The suspension is immediately cooled to −78 °C, and the precipitate is isolated by filtration, washed twice with cold pentane, and dried in vacuo at −50 °C: yield 1.22 g (61%); above −20 °C dec. IR (KBr, −20 °C): 1501, 1226 cm^{-1} (C_2H_2). ^{1}H NMR (THF-d_8, −80 °C): δ 7.3 (m, 30 H, PPh_3), 5.63 (d, J(PH) = 18.4 Hz, 2 H, C_2H_2), 2.30 (m, 4 H), 2.06 (m, 4 H, C_2H_4). ^{13}C NMR (THF-d_8, −80 °C): δ 137.2 (6 C), 134.3 (6 C), 129.95 (6 C), 129.0 (6

C, PPh_3), 85.5 (m, J(CH) = 210 Hz, 2 C, C_2H_2), 56.2 (4 C, C_2H_4). ^{31}P NMR (THF-d_8, -80 °C): δ 38.7. Anal. Calcd for $C_{42}H_{40}Ni_2P_2 \cdot C_4H_{10}O$ (724 + 74.1): C, 69.21; H, 6.31; Ni, 14.71; O, 2.00; P, 7.76. Found: C, 70.39; H, 6.48; Ni, 15.11; P, 7.86.

$(Ph_3P)_2Ni(C_2H_2)$ (6). See ref 9.

$(Ph_3P)_2Ni(C_2D_2)$ (6a). Synthesis as for **6** with C_2D_2. IR (KBr): 1529 cm^{-1} (C_2D_2).

$\{(Ph_3P)_2Ni\}_2(\mu\text{-}C_2H_2)$ (7). The THF solutions (7 mL) of 609.3 mg (1.0 mmol) of **6** and 611.3 mg (1.0 mmol) of $(Ph_3P)_2Ni(C_2H_4)$ are combined at 0 °C. From the red reaction solution an orange precipitate slowly separates at 20 °C. After addition of 30 mL of ether the compound is filtered off, washed twice with ether, and dried in vacuo at 20 °C; yield 860 mg (72%). IR: 1368 cm^{-1} (μ-C_2H_2). δ(P): 23.4 (33850 scans). Anal. Calcd for $C_{74}H_{62}Ni_2P_4$ (1192.6): C, 74.56; H, 5.24; Ni, 9.85; P, 10.39. Found: C, 74.56; H, 5.22; Ni, 9.75; P, 10.41.

$\{(Ph_3P)_2Ni\}_2(\mu\text{-}C_2D_2)$ (7a). Synthesis as for **7**, starting with $(Ph_3P)_2Ni(C_2D_2)$ (**6a**). IR (KBr): 1316 cm^{-1} (μ-C_2D_2).

$(Et_3P)Ni(C_2H_4)(C_2H_2)$ (8). The yellow solution of 5.0 mmol of $(Et_3P)Ni(C_2H_4)_2$ in 20 mL of pentane is exposed to about 150 mL (6 mmol) of ethyne at -100 °C. Soon light yellow crystals separate, which are drained by means of a capillary, washed twice with cold pentane, and dried in high vacuo at -78 °C: yield 750 mg (65%); -60 °C dec; at -78 °C not stable for long; very soluble in pentane at -78 °C. ^1H NMR (THF-d_8, -80 °C): δ 7.11 (d, J(PH) = 4.0 Hz, 1 H), 6.48 (d, J(PH) = 27.0 Hz, 1 H, C_2H_2), 2.61 (s, 4 H, C_2H_4), 1.77 (m, 6 H, PCH_2), 0.96 (m, 9 H, CH_3). ^{13}C NMR (THF-d_8, -80 °C): δ 110.8 (1 C, J(PC) = 19.2 Hz, ^1J(CH) = 226 Hz, ^2J(CH) = 24 Hz, C_2H_2), 104.2 (1 C, J(PC) = 13.2 Hz, ^1J(CH) = 222.5 Hz, ^2J(CH) = 26 Hz, C_2H_2), 50.75 (2 C, C_2H_4), 17.7 (3 C, J(PC) = 22.5 Hz, PCH_2), 8.6 (3 C, CH_3). ^{31}P NMR (THF-d_8, -80 °C): δ 26.8. Anal. Calcd for $C_{10}H_{21}NiP$ (231.0): C, 52.00; H, 9.16; Ni, 25.42; P, 13.41. Elemental analysis has not been carried out because of the instability of the compound.

$\{(Et_3P)Ni(C_2H_4)\}_2(\mu\text{-}C_2H_2)$ (9). The orange-red solution of 924 mg (4.0 mmol) of **8** and the yellow solution of 4.0 mmol of $(Et_3P)Ni(C_2H_4)_2$, both in 15 mL of pentane, are combined at -50 °C. Upon standing at -78 °C fine yellow crystals separate, which are drained by a capillary, washed twice with cold pentane, and dried in vacuo at -50 °C: yield 785 mg (45%); mp 0 °C; 10 °C dec; very soluble in cold ether and pentane. ^1H NMR (THF-d_8, -30 °C): δ 5.67 ("d", 2 H, C_2H_2), 2.42, 2.30 (m, 4 H, C_2H_4), 1.72 (m, 12 H, PCH_2), 0.90 (m, 18 H, CH_3). ^{13}C NMR (THF-d_8, -30 °C): δ 79.6 (m, 2 C, ^1J(CH) = 209 Hz, C_2H_2), 50.2 (4 C, C_2H_4), 18.3 (m, 6 C, PCH_2), 8.65 (6 C, CH_3). ^{31}P NMR (THF-d_8, -30 °C): δ 23.3. Anal. Calcd for $C_{18}H_{40}Ni_2P_2$ (435.9): C, 49.60; H, 9.25; Ni, 26.94; P, 14.21. The product analyzed contained 2/3 cocrystallized cdt according to its ^1H NMR spectrum. Anal. Calcd for $C_{18}H_{40}Ni_2P_2 \cdot C_8H_{12}$: C, 57.40; H, 9.63; Ni, 21.58; P, 11.39. Found: C, 57.55; H, 9.45; Ni, 21.68; P, 11.27.

$(Et_3P)Ni(C_2H_2)_2$ (10). The yellow solution of 5.0 mmol of $(Et_3P)Ni(C_2H_4)_2$ in 20 mL of pentane is exposed to ethyne (400 mL) in excess at -100 °C, and the reaction mixture is left at -78 °C for 24 h. The color slowly changes from light yellow to orange-red, and small yellow-brownish plates form, eventually at -100 °C, which are isolated as described above and dried in vacuo at -40 °C: yield 650 mg (57% Ni; purity 80%, rest $(Et_3P)Ni(C_2H_4)(C_2H_2)$ (**8**)); decomposition with *detonation at 0 °C*; moderately soluble in pentane, ether, and THF. ^1H NMR (THF-d_8, -80 °C): δ 7.10 (d, J(PH) = 3.3 Hz, 2 H), 6.15 (d, J(PH) = 28.5 Hz, 2 H, C_2H_2), 1.8 (m, 6 H, PCH_2), 0.95 (m, 9 H, CH_3). ^{13}C NMR (THF-d_8, -80 °C): δ 104.4 (2 C, J(PC) = 16.9 Hz, ^1J(CH) = 232 Hz, ^2J(CH) = 28 Hz, C_2H_2), 95.8 (2 C, J(PC) = 13.3 Hz, ^1J(CH) = 227 Hz, ^2J(CH) = 28.5 Hz, C_2H_2), 18.2 (3 C, J(PC) = 23.2 Hz, PCH_2), 8.7 (3 C, CH_3). ^{31}P NMR (THF-d_8, -80 °C): δ 29.4. Anal. Calcd for $C_{10}H_{19}NiP$ (228.9): C, 52.46; H, 8.37; Ni, 25.64; P, 13.53. Found: C, 52.77; H, 7.86; Ni, 25.59; P, 13.71.

$(Et_3P)_2Ni(C_2H_2)$ (11). To a clear solution of 1.615 g (5.0 mmol) of $(Et_3P)_2Ni(C_2H_4)$[21] in 20 mL of pentane is added ca. 150 mL (6 mmol) of ethyne at -78 °C. The color of the reaction solution changes from yellow via orange back to yellow, and yellow cubes crystallize. The mother liquor is sucked off by means of a capillary, the crystals are washed twice with cold pentane and dried in vacuo at -30 °C; yield 1.06 g (66%); mp -15 °C; moderately soluble in cold pentane. ^1H NMR (THF-d_8, -80 °C): δ 6.75 (m, 2 H, C_2H_2), 1.60 (m, 12 H, PCH_2), 1.02 (m, 18 H, CH_3). ^{31}P NMR (THF-d_8, -30 °C): δ 24.7. Anal. Calcd for $C_{14}H_{32}NiP_2$ (321.1): C, 52.37; H, 10.05; Ni, 18.29; P, 19.29. Found: C, 52.29; H, 10.20; Ni, 18.38; P, 19.21.

$\{(Et_3P)_2Ni\}_2(\mu\text{-}C_2H_2)$ (12). The pentane solutions (7 mL) of 642 mg (2.0 mmol) of **11** and 646 mg (2.0 mmol) of $(Et_3P)_2Ni(C_2H_4)$ are combined at -30 °C, and the orange-red reaction solution is left at this temperature for 1 h. The solution is cooled to -90 °C until crystallization starts. At -78 °C orange crystals are slowly obtained, which are drained, washed twice with cold pentane, and dried in vacuo at -30 °C: yield 690 mg (56%); mp 20 °C; very soluble in cold ether and pentane. MS (70 eV, 70 °C): m/z (% rel intens) 614 (M^+, 1), 496 ($M - PEt_3^+$, 2), 294 ($(Et_3P)_2Ni^+$, 30). ^1H NMR (THF-d_8, 27 °C): δ 4.84 (m, 2 H, C_2H_2), 1.57 (m, 24 H, PCH_2), 1.03 (m, 36 H, CH_3). ^{13}C NMR (THF-d_8, 38 °C): δ 89.5 (m, ^1J(CH) = 187 Hz, C_2H_2), 20.3 (m, PCH_2), 9.05 (m, CH_3). ^{31}P NMR (THF-d_8, 27 °C): δ 15.9. Anal. Calcd for $C_{26}H_{62}Ni_2P_4$ (616.1): C, 50.69; H, 10.14; Ni, 19.06; P, 20.11. Found: C, 50.78; H, 10.25; Ni, 18.77; P, 19.87.

$\{(Me_3P)Ni(C_2H_2)\}_2(\mu\text{-}C_2H_2)$ (13). To the yellow solution of 955 mg (5.0 mmol) of $(Me_3P)Ni(C_2H_4)_2$[23] in 20 mL of pentane (if obtained from 1.165 g (5.0 mmol) of Ni(cdt), ethene, and 380 mg of PMe_3, the liberated cdt is partly to be crystallized at -78/-100 °C and separated) is added 185 mL (7.5 mmol) of ethyne at -78 °C. The color of the solution remains yellow, and after a short time fine yellow crystals form, which are separated from the mother liquor, washed twice with cold pentane, and dried under high vacuum at -78 °C: yield 700 mg (80%); -60 °C dec with *explosion*. ^1H NMR (THF-d_8, -80 °C): δ 6.88 (d, J(PH) = 4.8 Hz, 2 H), 6.04 (d, J(PH) = 31.8 Hz, 2 H, C_2H_2), 5.75 (d, J(PH) = 21.9 Hz, 2 H, μ-C_2H_2), 1.28 (d, J(PH) = 7.1 Hz, 18 H, PMe_3). ^{13}C NMR (THF-d_8, -80 °C): δ 105.1 (J(CH) = 227 Hz, 2 C), 100.1 (J(CH) = 224 Hz, 2 C, C_2H_2), 71.3 (J(CH) = 218 Hz, 2 C, μ-C_2H_2), 17.8 (6 C, PMe_3). ^{31}P NMR (THF-d_8, -80 °C): δ -4.1. Anal. Calcd for $C_{12}H_{24}Ni_2P_2$ (347.7): C, 41.45; H, 6.96; Ni, 33.77; P, 17.82. Elemental analysis has not been carried out due to the instability of the compound.

$(Me_3P)Ni(C_2H_2)_2$ (14). The synthesis is carried out as for **13** but with 350 mL (14 mmol) of ethyne. After a short while yellow needles of **13** crystallize at -78 °C, and yellow cubes of **14** separate thereafter. **14** has not been isolated from **13**; total yield about 80% with respect to nickel, containing up to 50% **14**; -60 °C dec with *explosion*. ^1H NMR (THF-d_8, -80 °C): δ 7.00 (d, J(PH) = 4.2 Hz, 2 H), 6.18 (d, J(PH) = 31.7 Hz, C_2H_2), 1.42 (d, J(PH) = 7.4 Hz, 9 H, PMe_3). ^{13}C NMR (THF-d_8, -80 °C): δ 103.1 (J(CH) = 232 Hz, 2 C), 96.3 (J(CH) = 228 Hz, 2 C, C_2H_2), 17.55 (3 C, PMe_3). ^{31}P NMR (THF-d_8, -80 °C): δ -3.0. Anal. Calcd for $C_7H_{13}NiP$ (186.9): C, 44.99; H, 7.01; Ni, 31.42; P, 16.58. Elemental analysis has not been carried out because of separation problems and the instability of the compounds.

$(Me_3P)_2Ni(C_2H_2)$ (15). See ref 8.

$\{(MeO)_3P\}_2Ni(C_2H_2)$ (16). To a pentane solution (40 mL) of 4.0 mmol of tris(ethene)nickel(0), made from 932 mg (4.0 mmol of Ni, 5% cdt) of Ni(cdt) and ethene, is added 993 mg (8.0 mmol) of $P(OMe)_3$ at -30 °C, and the reaction mixture is filtered to remove insoluble impurities. After addition of about 110 mL (4.5 mmol) of ethyne at -78 °C, small light yellow needles separate from the yellow reaction solution. The mother liquor is removed through a capillary, and the crystals are washed twice with cold pentane and dried under high vacuum at -78 °C: yield 680 mg (51%); mp -30 °C dec. ^1H NMR (THF-d_8, -80 °C): δ 7.15 (C_2H_2), 3.50 (d, J(Ph) = 12 Hz, $P(OMe)_3$). ^{13}C NMR (THF-d_8, -80 °C): δ 119.6 (m, ^1J(CH) = 216 Hz, ^2J(CH) = 21 Hz, J(PC) = 49.2 Hz, J(P′C) = -11.4 Hz, C_2H_2), 50.7 (q, J(CH) = 145 Hz). ^{31}P NMR (THF-d_8, -80 °C): δ 166.7 (J(PP) = 29.1 Hz). Anal. Calcd for $C_8H_{20}NiO_6P_2$ (332.9): C, 28.86; H, 6.06; Ni, 17.64; P, 18.61. Found: C, 28.75; H, 6.66; Ni, 17.61; P, 18.46.

Reaction of 16 with $P(OPh)_3$: 253.1 mg (0.76 mmol) of solid **16** reacted with excess $P(OPh)_3$ to liberate 0.54 mmol of ethyne (71%).

$\{(PhO)_3P\}_2Ni(C_2H_2)$ (17). To an ethereal solution (15 mL) of 4.0 mmol $Ni(C_2H_4)_3$, made from 932 mg (4.0 mmol of Ni, 5% cdt) of Ni(cdt) and ethene is added at -30 °C 2.48 g (8.0 mmol) of $P(OPh)_3$, dissolved in 5 mL of ether, and the reaction mixture is filtered to remove insoluble impurities. After addition of about 110 mL (4.5 mmol) of ethyne at -78 °C, the color of the reaction solution slowly changes from yellow to red, and a light red precipitate is obtained, which is filtered off, washed twice with cold pentane, and dried in vacuo at -30 °C: yield 1.97 g (70%); 20 °C dec. IR (KBr): 1668 cm^{-1} (C_2H_2). ^1H NMR (THF-d_8, -30 °C): δ 7.25, 7.07 (m, Ph), 5.84 (m, C_2H_2). ^{13}C NMR (THF-d_8, -30 °C): δ 152.7, 130.1, 124.9, 122.2 (Ph), 112.0 (m, ^1J(CH) = 224 Hz, C_2H_2). ^{31}P NMR (THF-d_8, -30 °C): δ 145.5. Anal. Calcd for $C_{38}H_{32}NiO_6P_2$ (705.3): C, 64.71; H, 4.57; Ni, 8.32; P, 8.87. Found: C, 64.39; H, 5.08; Ni, 8.18; P, 8.69.

$\{(Me\text{-}2\text{-}C_6H_4O)_3P\}_2Ni(C_2H_2)$ (18). Synthesis was as for **17** but with 2.82 g (8.0 mmol) of $(Me\text{-}2\text{-}C_6H_4O)_3P$ as phosphite component. Upon addition of ethyne, the light yellow reaction solution changes its color to light orange, and a light yellow microcrystalline precipitate is obtained. After separation from the mother liquor by means of a capillary, the product is washed twice with cold pentane and dried in vacuo at -30 °C: yield 1.33 g (42%); 15 °C dec. IR (KBr): 1665 cm^{-1} (C_2H_2). ^1H NMR (THF-d_8, -30 °C): δ 7.25, 7.12 (m, C_6H_4O), 5.53 (m, C_2H_2), 2.07 (s, Me). ^{31}P NMR (THF-d_8, -30 °C): δ 146.1. Anal. Calcd for $C_{44}H_{44}NiO_6P_2$ (789.5): C, 66.94; H, 5.62; Ni, 7.44; P, 7.85. Found: C, 66.61; H, 5.92; Ni, 7.45; P, 7.80.

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$({}^tBuN{\equiv}C)_2Ni(C_2H_2)$ **(19).** The red solution of 816.5 mg (1.0 mmol) of $Ni_4({}^tBuNC)_7$ in 20 mL of ether (obtained and filtrated at 20 °C) is cooled to −50 °C. Upon addition of 83.1 mg (1.0 mmol) of ^{t}BuNC and about 150 mL (6 mmol) of ethyne, the red lightens slightly. After a few minutes yellow-brownish needles form, which are separated from the mother liquor, washed twice with cold pentane, and dried in vacuo: yield 622 mg (62%); above 0 °C dec. ^1H NMR (THF-d_8, −30 °C): δ 6.57 (C_2H_2), 1.45 (CH_3). ^{13}C NMR (THF-d_8, −30 °C): δ 157.5 ($N{\equiv}C$), 115.2 (d, $J(CH) = 212$ Hz, C_2H_2), 56.25 (CMe_3), 30.7 (CH_3). Anal. Calcd for $C_{12}H_{20}N_2Ni$ (251.0): C, 57.42; H, 8.03; N, 11.16; Ni, 23.39. Found: C, 57.60; H, 7.58; N, 11.38; Ni, 23.44.

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Organometallic Photochemistry in Thin Polymeric Films. Photoimaging

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Abstract: Dark green polymeric films of poly[(vbpy)Re$(CO)_3]_2$ have been prepared on electrode surfaces by reductive electropolymerization of [(vbpy)Re$(CO)_3$Cl]. Visible photolysis of the films immersed in CCl_4 leads to the cleavage of the metal–metal bond and formation of yellow poly[(vbpy)Re$(CO)_3$Cl] by photochemically well-defined processes. On the basis of the photochemistry, yellow-on-green images can be created in the films. They can be erased in a subsequent electrochemical reduction step, which re-forms the green dimer in 70% yield. The images can be developed further by allowing the unreacted dimer to react with appropriate organic oxidants or with Ag^+, which leads to the deposition of metallic silver in the dark areas of a light-generated pattern. Further deposition of silver can be carried out selectively in these unexposed regions by electrochemical reduction of Ag^+ in an external solution.

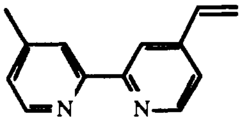
We report here the preparation and photochemical properties of electrode-bound, thin polymeric films in which there are molecular units containing metal-to-metal bonds. A goal of the work was to develop a reversible photoimaging system based on a well-established metal–metal bond cleavage reaction in solution (eq 1).[1,2] The underlying strategy was to combine photochemically

$$(CO)_5MnMn(CO)_5 \overset{h\nu}{\rightleftarrows} 2Mn(CO)_5{}^\bullet \xrightarrow{CCl_4} 2Mn(CO)_5Cl \tag{1}$$

$$2Mn(CO)_5Cl \xrightarrow{2e^-} Mn_2(CO)_{10} + 2Cl^- \tag{2}$$

induced halogen abstraction with electrochemical reduction (eq 2) as a means of returning the system to the metal–metal bonded state. We felt that a combination of the two, but in the translationally restricted environment of a polymeric film, could provide the basis for a sequential photochemical–electrochemical write–erase cycle.

The system chosen for study was a film-based analogue of [(bpy)Re$(CO)_3$Cl] (bpy is 2,2′-bipyridine). In earlier work it was shown that well-defined films of poly[(vbpy)Re$(CO)_3$Cl] (vbpy is 4-methyl-4′-vinyl-2,2′-bipyridine) can be formed on electrode surfaces[3] by using what are, by now, standard reductive electropolymerization techniques.[4] In the earlier work it was shown that many of the chemical and physical properties of the metal complex sites are retained in the film environment. In addition, polymeric films containing the metal–metal bonded dimer, poly[(vbpy)Re$(CO)_3]_2$, can be prepared by further electrochemical reduction of poly[(vbpy)Re$(CO)_3$Cl].



(vbpy)

Experimental Section

The electropolymerization and electrochemical experiments and some of the photochemical experiments were carried out in a Vacuum/Atmospheres glovebox with a slow, continuous flow of fresh nitrogen.

Materials. Acetonitrile (Burdick and Jackson, UV-grade, distilled in glass) and methylene chloride (Aldrich, Gold Label) were opened and stored in the glovebox and used as received. Small amounts (~20 mL) of carbon tetrachloride (Fisher) and 1,2-difluorobenzene (Aldrich, 98%) were purged with N_2 before being sealed and brought into the glovebox. Both carbon tetrachloride and 1,2-difluorobenzene (DFB) were purified by passage down a column of activated alumina. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was precipitated from water by mixing aqueous solutions containing stoichiometric amounts of tetra-*n*-butylammonium bromide and KPF_6 (both from Aldrich). The resulting precipitate was recrystallized twice from ethanol, dissolved in a minimum amount of acetonitrile, filtered to remove solid impurities, and precipitated into ether. The resulting white solid was washed with ether and dried in vacuo at 50 °C for 78 h. The syntheses of *fac*-[(vbpy)Re$(CO)_3$Cl],[3] [(bpy)Re$(CO)_3]_2$[5a] (bpy is 2,2′-bipyridine), and [(4,4′-dmbpy)Re$(CO)_3]_2$[5b] (4,4′-dmbpy is 4,4′-dimethyl-2,2′-bipyridine) are reported elsewhere. $AgPF_6$, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

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