

Novel α,β -C,C-Coupling Reaction of 1-Alkynyl Groups via I_2 Oxidation at Nickelate(II) Centers

Hans-F. Klein,* Monika Heiden, Mengzhen He, and Thomas Jung

Institut für Anorganische Chemie der Technischen Hochschule Darmstadt, Petersenstrasse 18,
D-64287 Darmstadt, FRG

Caroline Röhr

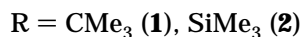
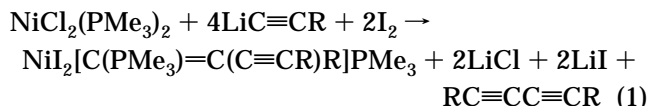
Institut für Anorganische und Analytische Chemie der Universität Freiburg, Albertstrasse 21,
D-79104 Freiburg, FRG

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Summary: C,C-coupling of $RC\equiv C^-$ ligands ($R = Me_3C, Me_3Si$) coordinated to Nast-type nickelate centers is initiated by I_2 and regioselectively steered by trimethylphosphine to afford the (1-(trimethylphosphonio)- σ -vinyl)nickel complexes $NiI_2[C(PMe_3)=C(C\equiv CR)R]PMe_3$.

Platinum-group metals are known to initiate C,C-coupling of 1-alkynes. For linear oligomerizations, Pt(II) complexes are efficient homogeneous catalysts,¹ while alkynyl groups in the presence of nickel² or palladium³ are trimerized in stoichiometric reactions.

We have discovered a new type of oxidative coupling reaction by reacting iodine with alkynylnickelate(II) complexes in the presence of trimethylphosphine, which selectively affords metal-coordinated 1-(trimethylphosphonio)- σ -vinyl groups:



The novel 1-buten-3-yn-1-ynickel complexes **1** and **2**, when crystallized from pentane, form orange-brown crystals, which under argon decompose above 160 °C, turning black.⁴ Spectroscopic data are compatible with square-planar coordination of nickel (16 valence electrons). The phosphonio group is attached to the α -C atom of the butenylnyl ligand and thereby subject to the steric demand of neighboring groups in the coordination plane, even when it is rotated perpendicular with respect to that plane. We have verified this orientation in the crystal for complex **1** (see Figure 1) and likewise for complex **2**.⁵

In the frame of C atoms no conjugational effects within the 2-(alkynyl)vinyl ligands are recognized. The distances C1–C2 and P–C1 in particular correspond well with a double and a single bond, respectively (Figure 1). Both bond lengths exclude participation of

an ylene form.⁶ Therefore, **1** must be formulated as a phosphoniumnickelate zwitterion. An additional polarization of the iodo ligands by the phosphonium ion is indicated by considerable narrowing of the ideally stretched angle I1–Ni–I2 to 163.3(1)° (168.2(2)° in **2**). As far as we are aware, compounds **1** and **2** are the first

(4) Synthesis of **1** and **2**: Under argon $NiCl_2(PMe_3)_2$ (850 mg, 3.0 mmol) and (3,3-dimethylbutynyl)lithium (1060 mg, 12.0 mmol) in 60 mL of THF were stirred for 10 h. A solution of I_2 (1520 mg, 6.0 mmol) in 20 mL of THF was added dropwise within 10 min. The volatiles were removed in vacuo and the residue was extracted with 80 mL of pentane over a sintered-glass disk (G 3). At -27 °C from 40 mL of pentane, crystals were obtained, which were isolated by decantation and washing with refluxing pentane under reduced pressure at -20 °C; yield 750 mg of **1** (40% with respect to nickel). **1**: black needles; mp 185–187 °C. Anal. Calcd for $C_{18}H_{36}I_2NiP_2$ (mol wt 626.9): C, 34.5; H, 5.8. Found: C, 34.8; H, 6.2. 1H NMR (200 MHz, C_6D_6 , 279 K): δ -($CCCH_3$) 1.01 (s, 9 H); δ ($PCCH_3$) 1.29 (d, $^2J(PH) = 8.4$ Hz, 9 H); δ (P^+CH_3) 1.97 (d, $^2J(PC) = 13.4$ Hz, 9 H); δ ($CCCH_3$) 2.31 (s, 9 H). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6 , 279 K, atom numbering as in Figure 1): δ (PCH_3) 14.4 (d, $^1J(PC) = 55.9$ Hz); δ (PCH_3) 17.5 (d, $^1J(PC) = 27.5$ Hz); δ (CCH_3) 27.8, 30.7; δ (CCH_3) 31.7; δ ($C5$) 40.9 (dd, $^3J(PC) = 23.0$ Hz, $^4J(PC) = 4.4$ Hz); δ ($C3$) 81.1 (dd, $^3J(PC) = 24.0$ Hz, $^4J(PC) = 12.0$ Hz); δ ($C4$) 101.4; δ ($C1$) 131.2 (dd, $^1J(PC) = 102.0$ Hz, $^2J(PC) = 14.4$ Hz); δ ($C2$) 145.5 (d, $^2J(PC) = 2.7$ Hz). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6 , 279 K, H_3PO_4): δ (NiP) -24.4 (d, $^3J(PP) = 15.8$ Hz, 1 P); δ (C^{P^+}) 5.4 (d, $^3J(PP) = 15.8$ Hz, 1 P). MS (FD, 0–15 mA; m/e (^{58}Ni) (%)): 626 (100), M; 499 (12), M – I. **2**: black needles; 27% yield; mp 153–156 °C. Anal. Calcd for $C_{16}H_{36}I_2NiP_2Si_2$ (mol wt 626.9): C, 29.16; H, 5.51. Found: C, 29.79; H, 5.46. 1H NMR (300 MHz, THF- d_6 , 279 K): δ ($SiCH_3$) 0.00 (s, 9 H); δ ($SiCH_3$) 0.56 (s, 9 H); δ ($PCCH_3$) 1.24 (d, $^2J(PH) = 8.3$ Hz, 9 H); δ (P^+CH_3) 2.23 (d, $^2J(PC) = 13.6$ Hz, 9 H). $^{13}C\{^1H\}$ NMR (75 MHz, THF- d_6 , 279 K, numbering of the C_4 chain as in Figure 1): δ ($SiCH_3$) -0.1 , 0.4; δ (PCH_3) 13.6 (d, $^1J(PC) = 53.2$ Hz); δ (PCH_3) 17.0 (d, $^1J(PC) = 27.4$ Hz); δ ($C4$) 101.1; δ ($C3$) 106.7 (dd, $^3J(PC) = 31.7$ Hz, $^4J(PC) = 14.5$ Hz); δ ($C2$) 141.6 (d, $^2J(PC) = 10.8$); δ ($C1$) 166.0 (d, $^1J(PC) = 108.7$ Hz, $^2J(PC) < 2$ Hz); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6 , 279 K, H_3PO_4): δ (NiP) -23.8 (d, $^3J(PP) = 19.7$ Hz, 1 P); δ (C^{P^+}) 15.9 (d, $^3J(PP) = 19.7$ Hz, 1 P). MS (FD, 0–15 mA; m/e (^{58}Ni) (%)): 658 (100), M; 531 (12), M – I.

(5) Crystal data for **1**, $C_{18}H_{36}I_2NiP_2$ ($M_r = 626.9$): black rods, crystal dimensions 0.29 × 0.25 × 0.31 mm, monoclinic, space group $P2_1$ (No. 4), $a = 13.733(2)$ Å, $a = 13.733(2)$ Å, $b = 8.826(1)$ Å, $c = 11.468(2)$ Å, $\beta = 106.74(9)^\circ$, $V = 1333.0(3)$ Å³, $Z = 2$, $d_{\text{calcd}} = 1.562$ g/cm³, $\mu = 3.163$ mm⁻¹. Data collection and refinement details: Philips PW1100 diffractometer, Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation, graphite monochromator, 293(1) K, ω - 2θ scanning technique. A total of 2648 unique reflections with $5.4^\circ \leq 2\theta \leq 50.0^\circ$ were collected, and 2517 were considered observed. Values ($R = 0.0655$, $wR2 = 0.1686$) are based on those reflections with $I^2 > 2\sigma(I^2)$. Crystal data for **2**, $C_{16}H_{36}I_2NiP_2Si_2$ ($M_r = 659.1$): black rods, crystal dimensions 0.45 × 0.31 × 0.23 mm, monoclinic, space group $P2_1/c$ (No. 14), $a = 21.686(7)$ Å, $b = 10.451(3)$ Å, $c = 13.117(4)$ Å, $\beta = 98.72(7)^\circ$, $V = 2938.0(2)$ Å³, $Z = 4$, $d_{\text{calcd}} = 1.490$ g/cm³, $\mu = 2.951$ mm⁻¹. Data collection and refinement details: Philips PW1100 diffractometer, Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation, graphite monochromator, 293(1) K, ω - 2θ scanning technique. A total of 1909 unique reflections with $5^\circ \leq 2\theta \leq 35^\circ$ were collected, and 1797 were considered observed. Values ($R = 0.0804$, $wR2 = 0.2087$) are based on those reflections with $I^2 > 2\sigma(I^2)$. Molecules of **2** and **1** show similar structures; however, distinction of P2 and Si2 was not possible in **2**.

(6) This feature of **1** is at variance with a diiron complex containing an α -phosphoniovinyl ligand which is metalated also at the β -C atom: Carty, A. J.; Taylor, N. J.; Paik, H. N.; Smith, W.; Yule, J. G. *J. Chem. Soc., Chem. Commun.* **1976**, 41.

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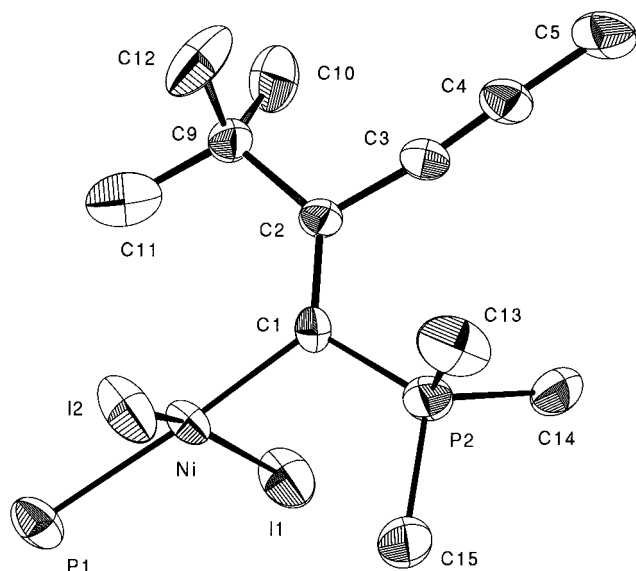


Figure 1. Molecular structure of **1** in the crystal form. Methyl groups at C5 and P1 show rotational disorder and have been omitted for the sake of clarity. Important distances (pm) and angles (deg): Ni–I1 = 252.5(2), Ni–I2 = 252.3(2), Ni–C1 = 192(2), Ni–P1 = 224.3(4), P2–C1 = 179(1), C1–C2 = 136(2), C2–C3 = 148(2), C3–C4 = 121(2), C4–C5 = 146(2); I1–Ni–I2 = 163.3(1), C1–Ni–P1 = 176.7(4), C2–C1–P2 = 118(1), P2–C1–Ni = 116(1), C1–C2–C3 = 120(1), C2–C3–C4 = 173(1).

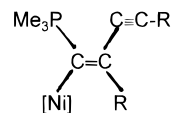
examples within the platinum group showing monodentate α -phosphonio- σ -vinyl groups.⁷ These are likely to originate from vinylidene intermediates which undergo nucleophilic attack by trimethylphosphine. Although access to the α -C atom is hindered by two iodo ligands, the small trimethylphosphine can be attached with the expected selectivity and without subsequent rearrangement.⁸

As the first step of the reaction sequence, the well-known oxidative cleavage of a Ni–C bond produces iodoalkyne molecules and Ni–I functions. With neutral alkynyl(trimethylphosphine)nickel iodides under these conditions a linear trimerization of alkynyl groups² is

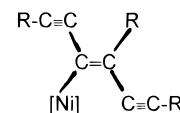
(7) With Pt^{II} a cationic complex of this type has been described: Dema, A. C.; Li, X.; Lukehart, C. M.; Owen, M. D. *Organometallics* **1991**, *10*, 1197.

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observed exclusively. Combining dialkynylbis(trimethylphosphine)nickel with iodoalkyne gives the trimerization product together with **1** or **2**, while in reactions according to eq 1 trimerization is suppressed. By steric control of substituents (R = CMe₃, SiMe₃) the observed regioselectivities turn out to be opposite:



[Ni] = *trans*-NiI₂(PMe₃); R = CMe₃, SiMe



[Ni] = *trans*-NiI(PMe₃)₂

Reduction of the steric demand of alkynyl groups, e.g. use of the phenylethynyl anion in a reaction according to eq 1, leads to mixtures of isomers depending on reaction temperature and concentrations. Selectivity with respect to two alternative products appears to be steered by the activity of nucleophiles, because compound **2** is also formed from different educts with a similar selectivity. Instead of the one-pot synthesis with an optimized stoichiometry according to eq 1, one can also start from *trans*-dialkynylbis(trimethylphosphine)-nickel and 2 mol of 1-iodoalkyne generated *in situ*,⁹ which affords an 89% yield of **2** (with respect to nickel).¹⁰ In both reactions metal-free butadiyne is formed at the expense of yields with respect to alkynyl reagent. With fewer equivalents of alkynyl/I₂ per nickel than are required in eq 1, the title reaction is suppressed, and the oxidative trimerization reaction² is activated. On the other hand, additional equivalents of iodine give rise to increasing amounts of NiI₃(PMe₃)₂¹¹ as a byproduct.

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Supporting Information Available: Tables of crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **1** and **2** (12 pages). Ordering information is given on any current mast-head page.

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