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Formation of Phosphirenes by Phosphinidene Group-Transfer Reactions from (dtbpe)Ni═P(dmp) to Alkynes

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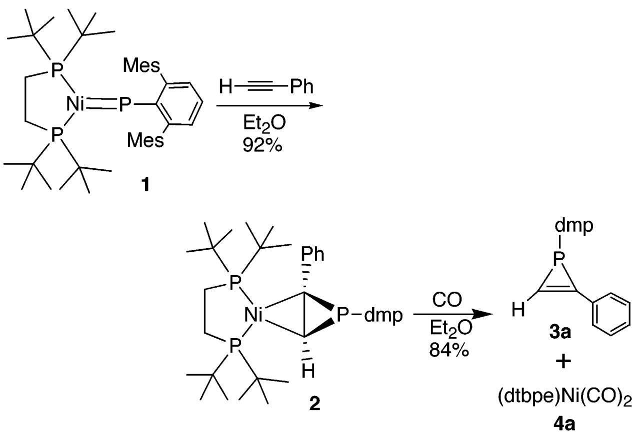
A valuable synthetic tool in organophosphorus chemistry has been the ability to generate phosphinidene ("PR") fragments with the aid of transition metals.[1] Isolated transition-metal−phosphinidene complexes are relatively rare, typically limited to early metals in high oxidation states.[2] Our preparation of the nickel complex (dtbpe)Ni═P(dmp) (**1**; dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane; dmp = 2,6-dimesitylphenyl) demonstrated the stability of terminal, late-transition-metal phosphinidene species,[3] and subsequently several examples of group 8 and 9 phosphinidene complexes have appeared.[4] Interesting recent reports by Carty and coworkers detail examples of stable, amino-substituted phosphinidene complexes for group 7−9 transition metals, some of which exhibit reaction chemistry involving intermolecular group transfer of the phosphinidene ligand.[5,6]

We have observed that **1** reacts with ethene, via an intermediate [2 + 2] cycloadduct, to effect phosphinidene transfer to the olefin with clean production of (2,6-dimesitylphenyl)phosphirane.[7] Herein we detail the results of a study of group-transfer reactions of **1** with alkynes that provide a general synthetic route to phosphirenes and the isolation and structural characterization of a unique olefin-bound phosphirene adduct of nickel.

Scheme 1



Reaction of ether solutions of **1** with phenylethyne at −35 °C results in formation of (dtbpe)Ni{η^2(*C*,*C*)-cyclo-CH═C(Ph)P(dmp)} (**2**), isolated as yellow crystals in 92% yield (Scheme 1).[8,9] Formulation of **2** as a π complex is consistent with its ^{1}H and ^{31}P NMR spectra, which indicate three inequivalent phosphorus environments in the square-planar complex with small P−P couplings (5.0, 6.0 Hz) between the dtbpe ligand and the −P(dmp) fragment, indicating that the latter is not coordinated to nickel. For comparison, the cationic nickel phosphido salts [(dtbpe)Ni{PH(dmp)}][PF$_6$] and [(dtbpe)Ni{P(CMe$_3$)$_2$}][PF$_6$] exhibit much larger P−P couplings (175, 186 Hz).[3] Only one diastereomer of **2** is observed, having the Ph and H ring substituents mutually syn, with the dmp group oriented anti with respect to Ni (clearly for steric reasons, as shown in Figure 1). Complex **2** is interesting, because all previously described examples of phosphirene ligands in metal complexes are coordinated through phosphorus in a dative fashion.[6,10] The

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(8) For complete experimental, spectroscopic, and crystallographic details, see the Supporting Information.

(9) An 8 mL diethyl ether solution of (dtbpe)Ni═P(dmp) (**1**, 112 mg, 0.144 mmol) was cooled to −35 °C. A cold solution of phenylethyne (14 mg, 0.144 mmol) in 2 mL Et_2O was added dropwise. The color slowly changed to yellow, and after 45 min of stirring, the solution was filtered and concentrated to about 3 mL. Cooling (−35 °C) of the concentrated solution overnight yielded pure yellow crystals of **2** (108 mg, 0.132 mmol, 92%). Spectroscopic and analytical data are given in the Supporting Information.

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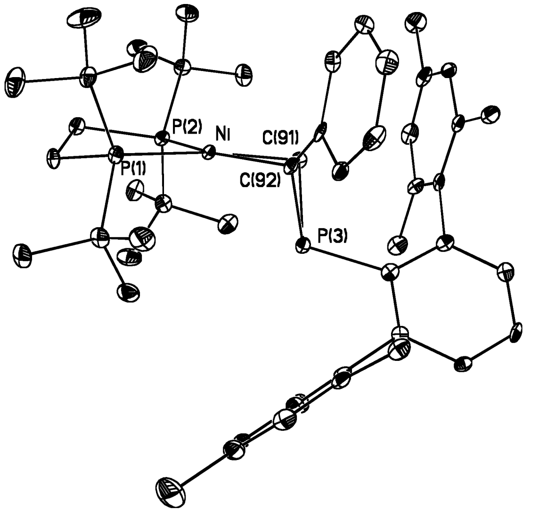


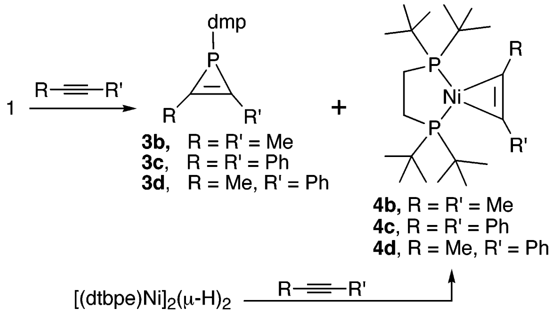
Figure 1. Perspective view of one enantiomer of **2** with thermal ellipsoids drawn at the 35% probability level. Hydrogen atoms have been omitted for clarity. Select bond lengths (Å) and angles (deg): Ni−C(91) = 1.917(5), Ni−C(92) = 1.960(5), P(3)−C(92) = 1.836(5), P(3)−C(91) = 1.840(5), C(91)−C(92) = 1.392(7), Ni−P(2) = 2.1567(15), Ni−P(1) = 2.1808(15), Ni−P(3) = 2.7245(15) Å; C(91)−Ni−C(92) = 42.1(2), C(91)−Ni−P(2) = 108.52(15), C(92)−Ni−P(1) = 115.40(15), C(91)−Ni−P(3) = 42.42(15), C(92)−Ni−P(3) = 42.33(15), C(92)−P(3)−C(91) = 44.5(2), P(2)−Ni−P(1) = 93.98(6).

only other example of “PR” group transfer from an isolated metal complex to an alkyne is that from Carty and co-workers, who found that the reaction of diphenylethyne with [Co(PN^{i}Pr$_2$)(CO)$_3$(PPh$_3$)][AlCl$_4$] forms P-bound [Co{cyclo-P(N^{i}Pr$_2$)C(Ph)═C(Ph)}(CO)$_3$(PPh$_3$)][AlCl$_4$].[6] This difference in binding modes might be attributable to steric constraints imposed by the bulky dtbpe ligand of **2**.

A single-crystal X-ray diffraction study of **2** confirmed the proposed structure, and a perspective view of **2** is shown in Figure 1 (only one of the two enantiomers, related in the crystal by an inversion center, is shown).[8,11] Complex **2** displays square-planar coordination at Ni with Ni−C bond lengths of 1.917(5) and 1.960(5) Å. The Ni−P(1) bond syn to the phenyl ring is slightly longer than the Ni−P(2) bond anti to the phenyl substituent (2.1808(15) vs 2.1567(15) Å). The phosphirene ligand is bound in a butterfly geometry with a Ni−P(3) distance of 2.7245(15) Å,[12] indicating there is effectively no bonding interaction. The C(91)−C(92) bond length at 1.392(7) Å is typical for a Ni−olefin species supported by the dtbpe ligand.[13]

We have observed that **1** reacts with small molecules having C═C and C═X double bonds to give [2 + 2] cycloadducts.[7] By analogy, the formation of **2** probably involves initial [2 + 2] cycloaddition of phenylethyne with the Ni═P double bond of **1** to afford a phosphametallacyclobutene intermediate that undergoes reductive elimination of the phosphirene (**3a**); trapping of the double bond of **3a** by Ni(0) would give **2**.

Scheme 2



Exposure of **2** to carbon monoxide results in liberation of the free phosphirene **3a**, which was isolated in 84% yield (Scheme 1).[8] The Ni was recovered as the dicarbonyl complex (dtbpe)Ni(CO)$_2$ (**4a**), identified by spectral comparison to an authentic sample prepared by the literature route.[13b] Spectroscopically, **3a** is very similar to the bound adduct, with the phosphorus resonance (δ −185.6) appearing as a singlet of frequency nearly identical with that found for **2** (δ −187.0) in the ^{31}P NMR spectrum; these are similar to literature values reported for other phosphirenes.[8,10] The methyl resonances in **3a** appear as two singlets of 2:1 intensity, demonstrating free rotation in the dimesitylphenyl group. This is in contrast to the mesityl-methyl resonances of **2**, which occur as three singlets (1:1:1), indicating hindered rotation about the C−C aryl bonds and fast rotation about the P−C(aryl) bond in the coordinated ligand on the NMR time scale.

Phosphinidene group transfer from **1** to alkynes appears to be quite general. **1** reacts with 2 equiv of 2-butyne, diphenylethyne, and 1-phenylpropyne to afford the corresponding phosphirenes **3b**−**d**, respectively, in isolated yields of 56−76% (Scheme 2).[15] When **1** is treated with 1 equiv of alkyne, a mixture of products and unreacted **1** is observed. The phosphirenes were characterized by NMR (^{1}H, ^{13}C, ^{31}P) and mass spectrometry.[8] Like **3a**, compounds **3b**−**d** have characteristic upfield ^{31}P NMR resonances (δ −169 to −175).

In these latter cases, the free alkynes are apparently better ligands for the “(dtbpe)Ni” fragment than is the olefinic moiety of the phosphirene ring, as the nickel-containing products were the alkyne adducts (dtbpe)Ni(η^2-MeC≡CMe) (**4b**), (dtbpe)Ni(η^2-PhC≡CPh) (**4c**), and (dtbpe)Ni(η^2-MeC≡CPh) (**4d**), as shown in Scheme 2. Complexes **4b**−**d** were characterized by spectroscopy

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(11) Crystal data for **2**: C$_{50}$H$_{71}$NiP$_3$, triclinic, $P\bar{1}$, a = 11.2060(11) Å, b = 13.0571(13) Å, c = 17.8952(17) Å, α = 79.464(2)°, β = 80.109(2)°, γ = 64.818(2)°, Z = 2, μ(Mo Kα) = 5.54 cm^{-1}, T = 100 K, V = 2316.6 (4) Å^3, λ = 0.71073 Å, D_c = 1.181 mg/mm^3. Of 18 806 data collected (yellow crystal, 2.21 ≤ θ ≤ 23.00°), 6452 were independent and observed with $I > 2\sigma(I)$. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were idealized and refined isotropically. $R(F)$ = 0.0702 and $R_w(F^2)$ = 0.1441.

(12) Nickel complexes with butterfly geometry are known for monomeric and polynuclear species: (a) Harrop, T. C.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chim. Acta* **2002**, *338*, 189. (b) Uhl, W.; Melle, S.; Frenking, G.; Hartmann, M. *Inorg. Chem.* **2001**, *40*, 750.

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(15) A representative procedure for the preparation of **3b**−**e** is given for **3b**. **2** (86 mg, 0.192 mmol) was dissolved in 10 mL of Et$_2$O and cooled to −35 °C. A cold 4 mL Et$_2$O solution of 2-butyne (42 mg, 0.776 mmol) was then added, and the solution was stirred for 30 min. The yellow-orange solution was then dried and extracted with petroleum ether, and the extract was filtered. cyclo-(dmp)PCMe═CMe was obtained by filtration of a petroleum ether solution through silica gel, concentrated to ca. 2 mL, and cooled to give pale yellow microcrystals (27 mg, 0.667 mmol, 56%).

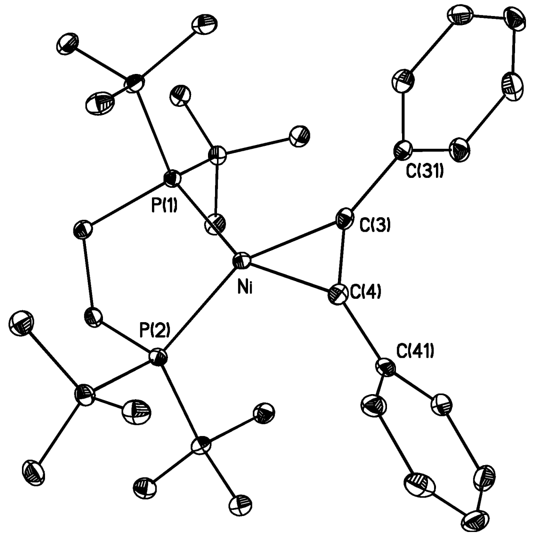
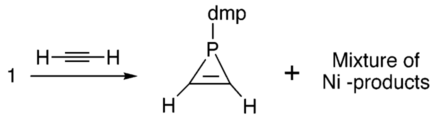


Figure 2. Perspective view of **4c** with thermal ellipsoids drawn at the 35% probability level. Hydrogen atoms have been omitted for clarity. Select bond lengths (Å) and angles (deg): Ni−C(4) = 1.878(2), Ni−C(3) = 1.897(2), Ni−P(2) = 2.1682(6), Ni−P(1) = 2.1726(6) Å; C(3)−Ni−P(1) = 114.29(7), C(4)−Ni−P(2) = 113.27(7), P(2)−Ni−P(1) = 92.62(2), C(31)−C(3)−Ni = 148.17(16), C(41)−C(4)−Ni = 144.86(17).

(^{1}H, ^{13}C, and ^{31}P NMR; infrared) and by elemental analysis.[8] Their identities were further confirmed by independent preparation by reaction of the alkynes with $[(dtbpe)Ni]_2(\mu\text{-}H)_2$, which acts as a Ni(0) synthon (Scheme 2).[14] Compounds **4b**,**c** show simple NMR spectra consistent with C_{2v} symmetry, and ν(CC) appears at 1806 and 1790 cm^{-1}, respectively, in the infrared region. Complex **4d** possesses inequivalent *tert*-butyl groups and dtbpe phosphorus nuclei (^{1}H and ^{31}P NMR) consistent with its C_s symmetry; ν(CC) appears at 1804 cm^{-1} in the infrared region. In the ^{1}H NMR spectrum of both **4b** and **4d**, the alkyne methyl groups show P−H coupling (~6 Hz) to the dtbpe ligand. The solid-state structures of one of these complexes, **4c**, was established via a single-crystal X-ray diffraction study (Figure 2) and confirms a square-planar geometry at nickel with Ni−C(3) and Ni−C(4) bond lengths of 1.878(2) and 1.897(2) Å, respectively, and a relatively short C(3)−C(4) bond (1.276(3) Å).[16] The structural parameters of **4c** are similar to those of a family of related nickel alkyne complexes $(dippe)Ni(C_2R_2)$ (dippe = 1,2-bis(diisopropylphosphino)ethane) prepared by Jones and co-workers.[17]

Ethyne reacts similarly with **1** to provide the parent phosphirene cyclo-(dmp)PCH═CH (**3e**) in 40% isolated yield (eq 1).[8] The ^{31}P NMR spectrum of **3e** shows the diagnostic downfield resonance for a phosphirene at δ −187, and the ^{1}H NMR spectrum shows strong P−H coupling for the ring protons ($^2J_{PH}$ = 28 Hz). This reaction, however, produces a complex mixture of nickel-containing products, which include the known nickel(0)−benzene adduct $[(dtbpe)Ni]_2(\mu\text{-}C_6H_6)$ and the nickel acetylene complex $(dtbpe)Ni(C_2H_2)$.[13,18]



(1)

In summary, we have shown that the late-transition-metal phosphinidene complex **1** readily reacts with a variety of alkynes via "PR" group transfer to form phosphirenes. This reactivity is similar to that reported for electrophilic transition-metal phosphinidene moieties. In one case, we are able to isolate an intermediate olefin-bound phosphirene adduct, which can be displaced from nickel by carbon monoxide. Recent calculations have suggested that the distinction between electrophilic and nucleophilic phosphinidene character may be more a function of the nature of the metal and its ligand set than of the PR fragment itself.[19] However, the limited sample of isolated phosphinidene complexes has provided little opportunity for testing this hypothesis. Additional studies of the highly reactive phosphinidene complex **1** are currently underway.

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Supporting Information Available: Text and tables giving experimental, spectroscopic, and crystallographic details; crystallographic data are given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Crystal data for **4d**: $C_{32}H_{50}NiP_2$, monoclinic, $P2_1/n$, a = 14.8436(9) Å, b = 11.2878(7) Å, c = 19.4216(11) Å, β = 110.7840(10)°, Z = 4, μ(Mo Kα) = 7.61 cm^{-1}, T = 100 K, V = 3042.4(3) Å^3, λ = 0.71073 Å, D_c = 1.212 mg/mm^3. Of 18 688 data collected (yellow crystal, $1.50 \le \theta \le 28.33°$), 7159 were independent and observed with $I > 2\sigma(I)$. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were idealized and refined isotropically. $R(F)$ = 0.0405 and $R_w(F^2)$ = 0.0795.

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