

**NICKEL(0) AND PALLADIUM(0) COMPLEXES WITH
(Z,Z)-Ph₂PCH₂C(*t*-Bu)=N-N=C(*t*-Bu)CH₂PPh₂.
ALKYNE-TO-ALKENYL CONVERSION IN
[Pd(MeOCOC≡CCOOMe){(Z,Z)-Ph₂PCH₂C(*t*-Bu)=N-N=C(*t*-Bu)CH₂PPh₂}**

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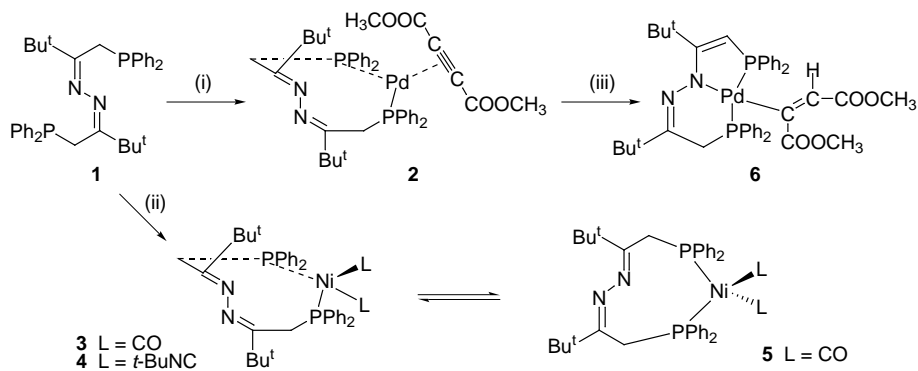
Novel zero-valent metal complexes [ML₂{(Z,Z)-Ph₂PCH₂C(*t*-Bu)=N-N=C(*t*-Bu)CH₂PPh₂}] (M = Ni, L = CO, *t*-BuNC) with the azine diphosphine chelating in a nine-membered ring were prepared. The nickel dicarbonyl complex was found to be in an equilibrium with its isomer containing (*E,Z*)-chelated azine diphosphine, the equilibrium being on the side of the (*Z,Z*)-isomer below 60 °C. A similar palladium complex (M = Pd, L₂ = CH₃OCOC≡CCOCH₃) prepared earlier was found to undergo a rearrangement with simultaneous alkyne-to-alkenyl conversion of the acetylenedicarboxylate dimethyl ester ligand.

Key words: Nickel; Palladium; Alkyne complexes; Chelates; P ligands; Phosphines; Azines; Bidentate ligands.

The azine diphosphine compound Ph₂PCH₂C(*t*-Bu)=N-N=C(*t*-Bu)CH₂PPh₂ (**1**) (Scheme 1), recently introduced by Shaw *et al.*¹, turned up to be a very versatile ligand towards transition metal centres. It can act as a two-, four- or six-electron donor coordinated in (P,P'), (P,N) or (P,N,P') modes in square planar, octahedral or trigonal bipyramidal environments²⁻⁷. Since the barrier for rotation around the C=N bond in azines is relatively low, the ligand is able and often was found to chelate various metals in (*E,Z*)-configuration. The possibility of chelation in (*Z,Z*)-configuration was therefore considered improbable until very recently. Shaw and co-workers have shown⁸ that gold(I), known to exhibit a broad range of L-Au-L bond angles, can accommodate the ligand in (*Z,Z*)-configuration, the P-Au-P' angle being 139.5°. Silver(I) and copper(I) complexes were also obtained. It was

shown recently that such (*Z,Z*)-chelating coordination is not limited to groups Ib metals and a zero-valent palladium complex **2** was prepared⁹.

Hereinafter we describe the reaction of the azine diphosphine **1** with a nickel(0) complex and isolation and characterization of complexes produced in which **1** also coordinates to nickel(0) in (*Z,Z*)-configuration. An equilibrium between (*Z,Z*)- and (*E,Z*)-chelated nickel dicarbonyl complexes was found whereas the known palladium complex **2** on standing in solution gives quantitatively a novel Pd(II) complex.



Reagents and conditions: (i) $\text{Pd}_2(\text{DBA})_3$ (DBA = dibenzylideneacetone) in toluene, then $(\equiv\text{CCOOMe})_2$; (ii) $[\text{Ni}(\text{cod})_2]$ in THF, then CO for **3**; $[\text{Ni}(\text{cod})_2]$ in diethyl ether, then *t*-BuNC for **4**; (iii) benzene or THF, 14 days standing

SCHEME 1

Reaction of bis(cycloocta-1,5-diene)nickel with azine diphosphine **1** followed by the reaction with carbon monoxide or *tert*-butyl isocyanide led to formation of novel complexes **3** or **4**, respectively. NMR spectra of both compounds strongly resemble those of complex **2**. For example, only one singlet was found in the ^{31}P NMR spectra, indicating the equivalence of the two phosphorus atoms; *tert*-butyl groups are also equivalent. The complexes **3** and **4** have been described by structures with (*Z,Z*)-chelating azine diphosphine, analogous to the structure of **2**. It should be mentioned here that dimeric dinuclear structures with the same composition but with two (*Z,Z*)-bridging ligands would also comply with the NMR data. Our assignment is based on (i) the known X-ray structure⁹ of **2** and close similarity between the NMR spectra of **3** and **4** and those of **2**, (ii) FAB mass spectrum of **3** which shows molecular ion of the compound at (*m/z*) 679, (iii) the result of cryoscopic molecular weight determination for **3** where the value of 719 was established. The CO-stretching frequencies of the carbonyl ligands in the infrared spectrum of **3** (1 942 and 2 002 cm^{-1}) have been compared

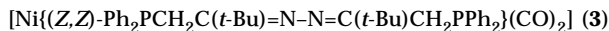
with the published¹⁰ $\nu(\text{CO})$ frequencies of $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$ and $[\text{Ni}(\text{CO})_2\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$ ($n = 2-4$) and place **1** close to 1,4-bis(diphenylphosphino)butane ($\nu(\text{CO})$ values for the latter complex with $n = 4$ are 1 940 and 1 995 cm^{-1}).

In the temperature range from ambient to 60 °C, the nickel dicarbonyl complex **3** was found to be in an equilibrium with another compound which displayed doublet of doublets with $^2J(\text{P,P}) = 13.2$ Hz in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, and inequivalent *tert*-butyl as well as methylene protons in the ^1H spectrum. Structure **5** containing chelating azine diphosphine in (*E,Z*)-configuration has been therefore assigned to this compound. The temperature dependence of the equilibrium constant of the isomerization, determined from the ratio of integrals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, could be described by the equation $\ln K = -935/T + 1.99$. This result shows that at least in one example of complex **3**, the (*Z,Z*)-configuration of the chelating azine diphosphine is preferred over the (*E,Z*)-configuration even at 60 °C, and that at ambient temperature only about a quarter of the total amount of the ligand is in the (*E,Z*)-configuration. It is not the kinetic control due to the barrier of rotation around the C=N bond that prevents the chelating azine diphosphine to adopt the (*E,Z*)-configuration in the complex but, instead, a thermodynamic equilibrium which is established in about an hour time. Under the same conditions, complex **4** was stable. The palladium complex **2** underwent a quantitative reaction in the course of two weeks at ambient temperature, leading ultimately to a novel orange-red complex **6**. Its ^{31}P NMR spectrum showed an AB system with $^2J(\text{P,P})$ coupling constant of 379 Hz indicating *trans*-arrangement of phosphine donor atoms. The value is close to that (361 Hz) of the ene-hydrazone complex with *trans*-vinyl ligand obtained by electrochemically induced transformation of **2** (ref.⁹) but the difference is much higher than the experimental error. Also, ^1H and ^{13}C NMR spectra of both compounds are very similar but definitely different from each other. FAB mass spectra show that the compounds are isomers. The most notable differences between the complexes were found in ^1H NMR spectra. The signal of vinyl proton in the ene-hydrazone complex with *trans*-vinyl ligand at 6.04 ppm is a doublet of doublets with couplings to both phosphorus atoms, as may be expected for the *trans*-vinyl proton. The signal of the vinyl proton in complex **6** at 5.22 ppm is a singlet. This fact together with those already mentioned above led us to assignment of an ene-hydrazone structure with *cis*-vinyl ligand to complex **6**. While the signal of methylene protons in the former compound is a complex multiplet due to inequivalence of the two protons, the corresponding signal in **6** is a doublet of doublets. This indicates rapid inversion of the

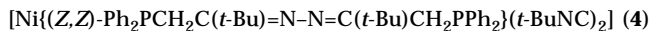
six-membered ring in **6** making thus the protons equivalent by the fast exchange on the NMR time scale. We were unable to slow down the inversion at $-30\text{ }^{\circ}\text{C}$.

EXPERIMENTAL

Syntheses of complexes and other manipulations were carried out in an argon atmosphere unless stated otherwise. Solvents were dried by refluxing over sodium/benzophenone, followed by distillation in an argon atmosphere. Azine diphosphine **1** (ref.¹), bis(cycloocta-1,5-diene)nickel¹¹ and complex **2** (ref.⁹) were prepared according to literature. *tert*-Butyl isocyanide (Aldrich) was used as supplied. Elemental analyses were carried out by the analytical services of the University of Leeds. Mass spectra with FAB ionization were recorded using a VG Autospec spectrometer with 8 kV acceleration. Fourier-transform infrared spectra were measured on a Bruker IFS 88 instrument in KBr discs. NMR spectra were recorded on a Varian UNITY 200 instrument, using hexamethyldisilane as internal standard for ^1H and ^{13}C nuclei, and 85% H_3PO_4 as external standard for ^{31}P nucleus. Spectra are given without signals of phenyl proton and carbon nuclei since these values are usually of little structural importance and are not reported in the literature.



Azine diphosphine **1** (1.85 g, 3.28 mmol) and bis(cycloocta-1,5-diene)nickel (0.90 g, 3.3 mmol) were dissolved in THF (50 ml) and carbon monoxide was passed through the solution under stirring for 2.5 h. The solution was filtered, volatiles were evaporated *in vacuo* and the product recrystallized from diethyl ether (7 ml) at $-18\text{ }^{\circ}\text{C}$. Yield 1.95 g (88%) of beige crystals. For $\text{C}_{38}\text{H}_{42}\text{N}_2\text{NiO}_2\text{P}_2$ (679.4) calculated: 66.76% C, 6.58% H, 3.89% N; found: 66.85% C, 7.10% H, 3.65% N. FAB MS, m/z : 679 (M^+), 623 ($\text{M}^+ - 2\text{ CO}$). IR ($400\text{--}4\ 000\text{ cm}^{-1}$): 510 vs, 606 m, 696 vs, 739 vs, 848 w, 867 m, 1 071 w, 1 115 s, 1 190 m, 1 203 m, 1 361 m, 1 477 s, 1 482 m, 1 613 m, 1 942 vs (CO), 2 002 vs (CO), 2 866 m, 2 902 m, 2 929 m, 2 969 s. ^{31}P NMR (81 MHz, C_6D_6): 36.5 s. ^1H NMR (200 MHz, C_6D_6): 0.87 s, 9 H ($3 \times \text{CH}_3$); 3.13 dd, 1 H, $^2J(\text{H},\text{H}) = 12.2$, $^2J(\text{P},\text{H}) = 10.3$ (CH_2); 4.22 dd, 1 H, $^2J(\text{H},\text{H}) = 12.2$, $^2J(\text{P},\text{H}) = 11.3$ (CH_2). ^{13}C NMR (50.3 MHz, C_6D_6): 29.2 s (CH_3); 34.6 d, $J(\text{P},\text{C}) = 2.2$ (CH_2); 39.5 s ($>\text{C}<$); 168.3 s ($\text{C}=\text{O}$), 199.5 t, $|^2J(\text{P},\text{C}) + ^4J(\text{P},\text{C})| = 5.0$ ($\text{C}=\text{NN}$).

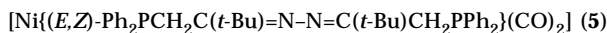


Azine diphosphine **1** (2.85 g, 5.05 mmol) and bis(cycloocta-1,5-diene)nickel (1.39 g, 5.05 mmol) were stirred in diethyl ether (40 ml) until solids dissolved. *tert*-Butyl isocyanide (0.84 g, 10.1 mmol) was added and the mixture was stirred overnight. The resulting green solution was filtered and concentrated to 15 ml. The product which separated on standing at $-30\text{ }^{\circ}\text{C}$ overnight was filtered off and dried *in vacuo*. Yield 3.36 g (84%) of yellow crystals. For $\text{C}_{46}\text{H}_{60}\text{N}_4\text{NiP}_2$ (789.6) calculated: 69.97% C, 7.66% H, 7.10% N; found: 69.65% C, 7.90% H, 7.15% N. IR ($400\text{--}4\ 000\text{ cm}^{-1}$): 510 vs, 602 w, 740 s, 751 m, 867 w, 1 027 vw, 1 086 m, 1 192 m, 1 215 m, 1 364 w, 1 390 w, 1 434 m, 1 459 w, 1 477 w, 1 584 w, 1 614 w, 2 011 vs, 2 060 vs, 2 868 w, 2 902 w, 2 927 m, 2 978 m, 3 048 w. ^{31}P NMR (81 MHz, C_6D_6): 36.9 s. ^1H NMR (200 MHz, C_6D_6): 0.87 s, 9 H ($3 \times \text{CH}_3$); 1.02 s, 9 H ($3 \times \text{CH}_3$); 3.42 dd, 1 H, $^2J(\text{H},\text{H}) = 11.7$, $^2J(\text{P},\text{H}) = 8.6$ (CH_2); 4.23 dd, 1 H, $^2J(\text{H},\text{H}) = 11.7$, $^2J(\text{P},\text{H}) = 8.6$ (CH_2). ^{13}C

NMR (50.3 MHz, C_6D_6): 29.6 s (CH_3); 31.4 s (CH_3); 35.9 s (CH_2); 39.3 s ($>C<$); 54.6 s ($>C<$); 166.3 t, ${}^2J(P,C) + {}^4J(P,C) = 5.3$ (C=NN); 168.2 s (C=NC).

Equilibrium Between **3** and **5**

Complex **3** (30 mg) and C_6D_6 (0.8 ml) were placed in an NMR tube which was then cooled to -78 °C and sealed off in vacuum. After warming up to ambient temperature, the complex dissolved giving colourless solution. The tube was then placed in NMR spectrometer and ${}^{31}P$ and 1H NMR spectra were recorded to check the purity. The temperature in the probe was then successively increased to 30, 40, 50, and 60 °C; at each temperature the sample was kept for 1 h before taking the ${}^{31}P$ spectrum. The spectra were recorded with a relaxation delay of 30 s, forty scans each. The sample was then cooled down in steps corresponding to the same temperature series as used for warming. Integration of signals gave relative amounts of **3** and **5**; an average of two values at a particular temperature was used. The temperatures were corrected using ethylene glycol as a chemical thermometer to 18.0 (ambient), 27.2, 37.6, 48.7, and 59.3 °C. The equation for the temperature dependence of the equilibrium constant was obtained by the least-squares fit of the data. 1H NMR spectrum of complex **5** was subtracted from the spectrum of the mixture at 59.3 °C.



${}^{31}P$ NMR (81 MHz, C_6D_6): 19.5, 21.7 (AB system, ${}^2J(P,P) = 13.2$). 1H NMR (200 MHz, C_6D_6): 0.67 s, 9 H ($3 \times CH_3$); 1.21 s, 9 H ($3 \times CH_3$); 3.00 d, 2 H, ${}^2J(P,H) = 10.2$ (CH_2); 3.19 d, 2 H, ${}^2J(P,H) = 8.0$ (CH_2).



Complex **2** (150 mg) was dissolved in benzene (15 ml) and the resulting colourless solution was left to stand at ambient temperature for two weeks during which time it gradually became orange. Evaporation of the solvent gave an orange-red solid quantitatively. The product was recrystallized from THF/*n*-heptane. FAB MS, m/z : 813 (M^{+}), 670 ($M^{+} - (CCOOMe)_2 - H$). IR (400–4 000 cm^{-1}): 485 m, 503 m, 534 m, 581 w, 738 s, 745 s, 853 w, 877 m, 1 000 w, 1 007 w, 1 027 w, 1 039 w, 1 102 m, 1 137 m, 1 160 s, 1 212 s, 1 277 m, 1 327 s, 1 387 w, 1 434 s, 1 477 s, 1 589 m, 1 705 vs, 1 713 vs, 2 947 m. ${}^{31}P$ NMR (81 MHz, C_6D_6): 27.5, 49.6 (AB system, ${}^2J(P,P) = 379$). 1H NMR (200 MHz, C_6D_6): 1.04 s, 9 H ($3 \times CH_3$); 1.92 s, 9 H ($3 \times CH_3$); 3.04 dd, 2 H, ${}^2J(P,H) = 11.2$, ${}^4J(P,H) = 2.2$ (CH_2); 3.35 s, 3 H (OCH_3); 3.51 s, 3 H (OCH_3); 4.70 dd, 1 H, ${}^2J(P,H) = 5.3$, ${}^4J(P,H) = 1.6$ (PCH=); 5.22 s, 1 H (CH=). ${}^{13}C$ NMR (50.3 MHz, C_6D_6): 22.00 d, $J(P,C) = 17.6$ (CH_2); 29.32 s (CH_3); 32.04 s (CH_3); 39.87 d, ${}^3J(P,C) = 2.4$ ($>C<$); 40.36 d, ${}^3J(P,C) = 15.1$ ($>C<$); 50.85 s (OCH_3); 50.87 s (OCH_3); 73.8 d, $J(P,C) = 54$ (PCH=); 123.99 t, ${}^3J(P,C) = 5.1$ (CH=); 147.78 s ($>C=$); 162.97 s (C=N); 174.33 s (C=N); 189.29 s (C=O); 189.69 s (C=O).

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