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Synthesis and Crystal Structure Analysis of Bis(η^5-cyclopentadienyl)-μ-[trifluoromethyl(oxodiphenylphosphino)acetylene]-dinickel(0)

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Upon reaction of nickelocene with the phosphinoacetylene $Ph_2PC{\equiv}CCF_3$ six products were isolated, one of which is a deep green solid whose formulation is $[(\eta^5\text{-}C_5H_5)Ni]_2\text{-}\mu\text{-}(Ph_2P(O)C{\equiv}CCF_3)$. The crystal and molecular structure of this complex has been determined from three-dimensional x-ray data collected by counter methods. The crystals are orthorhombic, space group *Pbca*, with eight molecules in a unit cell of dimensions $a = 25.286$ (2), $b = 10.427$ (2), and $c = 17.021$ (2) Å. Full-matrix least-squares refinement on F of the structure has led to a conventional R value of 0.040 for 1796 observed reflections. The binuclear complex contains two nickel atoms asymmetrically bridged by an acetylide moiety in π-bonding fashion with Ni–C distances falling into two distinct sets, 1.873, 1.896 (6) Å and 1.909, 1.920 (6) Å, and a Ni–Ni bond length of 2.365 (1) Å. Both nickel atoms are π bonded to the η^5-cyclopentadienyl groups with mean Ni–C and C–C lengths of 2.096 (8) and 1.402 (13) Å, respectively. The phosphinoacetylide has bond distances P═O = 1.473 (5), P—C(phenyl)(mean) = 1.802 (8), P—C(acetylide) = 1.774 (6), C—C(acetylide) = 1.472 (10), C≡C = 1.353 (9), C—F(mean) = 1.311 (12), and C—C(phenyl)(mean) = 1.386 (11) Å. The angles C≡C—CF_3 [140.7 (6)°] and P—C≡C [150.2 (5)°] are characteristic of a cis-bent geometry for the coordinated phosphinoacetylide.

Cyclopentadienylnickel carbonyl dimer, $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$, and nickelocene, $(\eta^5\text{-}C_5H_5)_2Ni$, react with acetylenes yielding the acetylene-bridged dimer $[(\eta^5\text{-}C_5H_5)Ni]_2(RC{\equiv}CR')$ (I) as major products.[3-5] However, with highly electrophilic acetylenes, cycloaddition of the alkyne to one cyclopentadienyl ring of nickelocene may occur leading to σ,π-norbornyl complexes (II).[6-10] While compounds of formulation I and II are quite stable and examples have been characterized structurally,[11,12] one could intuitively predict that both types should be susceptible to further reaction with acetylenes. For example, acetylene trimers and oligomers as well as organocobalt complexes result from reactions of the isoelectronic and isostructural cobalt analogues of I, $Co_2(CO)_6(RC{\equiv}CR')$, with additional alkyne[13] while acetylene insertion into M—C σ bonds (cf. II) is a well-established organometallic reaction. These predictions are substantiated by results[15] of a reexamination of the hexafluorobut-2-yne/nickelocene system where the new complexes $(\eta^5\text{-}C_5H_5)Ni[C_5H_5(CF_3C_2CF_3)_2]$, $[(\eta^5\text{-}C_5H_5)Ni(CF_3C_2CF_3)]_4$, and $(\eta^5\text{-}C_5H_5)_2Ni_3(CF_3C_2CF_3)_2$ appear to relate to the initial products of formulation I and II. Among several features of these interesting reactions which warrant attention are the role of the metal atom in the cycloaddition process and the fate of the displaced cyclopentadienyl ligand in the formation of the products I from $(\eta^5\text{-}C_5H_5)_2Ni$. In an attempt to gain insight into these processes, we have investigated the reactions of $(\eta^5\text{-}C_5H_5)_2Ni$ and $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ with the phosphinoalkynes $Ph_2PC{\equiv}CR$ (R = CF_3, Ph, *t*-Bu). Previous work[16] has demonstrated the utility of these ligands in allowing the isolation and characterization of model intermediate π complexes prior to oligomerization of the alkyne by metal carbonyls. With the less activated alkynes $Ph_2PC{\equiv}CR$ (R = Ph, *t*-Bu) evidence for –C≡C– and phosphorus coordination was found but cycloaddition was suppressed.[17] By contrast, six products have been isolated from the reaction of $Ph_2PC{\equiv}CCF_3$ with $(\eta^5\text{-}C_5H_5)_2Ni$ at room temperature including a derivative with a $\eta^1\text{-}C_5H_5$ ring[15] and a dinickel complex $[(\eta^5\text{-}C_5H_5)Ni]_2[Ph_2PCH{=}C(CF_3)C(PPh_2){=}C(CF_3)C_5H_5]_2$[18] containing a dimer derived from two displaced $C_5H_5^-$ ligands, which will be described in a subsequent publication.[19] In this paper we describe the synthesis and structural characterization of a species obtained on oxidation of one of the reaction products, namely, $[(\eta^5\text{-}C_5H_5)Ni]_2(Ph_2P(O)C{\equiv}CCF_3)$. This is the first acetylenic phosphine oxide π complex to be characterized structurally. Furthermore, our x-ray analysis provides precise details of molecular geometry for a complex of formulation I. Such information is highly relevant to an assessment of the influence of steric and electronic factors on the activation of the coordinated triple bond.

Experimental Section

Preparation. $(\eta^5\text{-}C_5H_5)_2Ni$ (1.9 g) was introduced into a Schlenk tube followed by 1.4 g of freshly distilled phosphine ligand.[20] Degassed benzene (~20 ml) was added and the dissolved components were allowed to react under N_2 for 2 h. The green mixture turned red, maroon, purple, and finally brown. At the end of the reaction, 5 ml of benzene was added and insolubles were filtered off with a filter stick. The solution was chromatographed on alumina giving eight bands. The first two bands were nickelocene and a free ligand. The next five bands, eluted with petroleum ether/benzene mixtures, contained products to be described in a subsequent publication.[15] The last green band, eluted with diethyl ether gave, after removal of solvent, deep green crystals of a complex with an analysis consistent with the formulation $(C_5H_5)_2Ni_2(Ph_2P(O)C_2CF_3)$, mp 150–151 °C. Anal. Calcd for $C_{25}H_{20}F_3Ni_2OP$: C, 55.56; H, 3.73; P, 5.74. Found: C, 55.27; H, 3.69; P, 5.63. Ir spectrum (Nujol mull) (cm^{-1}): 1564 vs (ν(C=C) of a μ-coordinated acetylene), 842 (m), 833 (s) (δ(C—H) of C_5H_5), 1203 (vs) (ν(P=O)). The absence of ν(C≡C) of the free ligand (2197 cm^{-1}), the appearance of an intense band typical of alkyne-bridge bimetallic species[21] at 1564 cm^{-1}, and the appearance of a new band in the P=O stretching region of the infrared spectrum suggested the presence of an acetylenic phosphine oxide coordinated in μ fashion to two nickel atoms. The NMR spectrum in C_6D_6 shows τ 1.85 (m), 2.72 (m) (phenyl H) and 4.94 (s) (C_5H_5) [the chemical shift of the cyclopentadienyl resonance is typical of η^5 ligands[9,10]]. The mass spectrum exhibits a parent ion at *m/e* 540. Fragmentation occurs by loss of C_5H_5Ni to give $[C_5H_5Ni(Ph_2P(O)C_2CF_3)]^+$ at *m/e* 417 or loss of ligand to give $[(C_5H_5)_2Ni_2]^+$ at *m/e* 246 in high abundance. The former ion then loses $CF_3C{\equiv}C$ and C_5H_5Ni giving intense ions at *m/e* 324, $[C_5H_5NiPh_2PO]^+$, and *m/e* 101, $[Ph_2PO]^+$, respectively. A structure analogous to that of $[(\eta^5\text{-}C_5H_5)_2Ni](Ph_2C_2)$[11] seemed likely and this is confirmed by our x-ray crystal structure analysis.

Collection and Reduction of the X-Ray Intensity Data. The dark green crystals were examined by Weissenberg and precession photography, and they showed systematic absences uniquely determining the space group *Pbca* (No. 61). Unit cell dimensions a = 25.286 (2), b = 10.427 (2), and c = 17.021 (2) Å were obtained by least-squares refinement of the setting angles of 12 general reflections accurately centered in a 3.5-mm diameter circular receiving aperture on a Hilger and Watts Y290 four-circle computer-controlled diffractometer (λ(Mo Kα) 0.71069 Å, T = 22 °C) equipped with a graphite monochromator. The calculated density of 1.610 g cm^{-3} for Z = 8 agrees with the measured density of 1.60 (1) g cm^{-3} by flotation in impure carbon tetrachloride, and $F(000)$ = 2208.

Diffraction data were collected from a well-formed dark green platelet with maximum dimensions 0.37 × 0.09 × 0.11 mm and mounted on a eucentric goniometer head with the a axis approximately parallel to the ϕ axis. Its six bounding faces were identified and their distances from an arbitrary crystal center were measured using a calibrated graticule in a binocular microscope. The θ–2θ scan technique and Mo Kα radiation were used to record the intensities of a unique octant of data within the limits $2 < 2\theta < 46°$. A symmetric scan range of 0.6° in 2θ, centered on the calculated peak position (λ(Mo Kα) 0.71069 Å), was composed of 60 steps of 1-s duration. Stationary-crystal, stationary-counter background counts (b_1, b_2) were measured for 15 s at the beginning and end of the scan range. Reflections for which the intensity of the diffracted beam exceeded 10 000 counts/s were automatically remeasured with aluminum foil attenuators inserted in order to be within the linear response range of the scintillation counter. The counter was located 200 mm from the crystal. The intensities of two standard reflections, monitored at 100-reflection intervals, fluctuated by less than 1.2% during data collection.

Data were corrected for Lorentz and polarization factors[22] [$1/Lp = (\sin 2\theta_s)(\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s)$ where $2\theta_s$ and $2\theta_m$ are the diffraction angles at the sample crystal and monochromator, respectively] and then for absorption[23] (μ(Mo Kα) = 17.87 cm^{-1}) using Gaussian integration. Maximum and minimum values of transmission coefficients are 0.8748 and 0.8351, respectively. Standard deviations were assigned to intensity values according to $\sigma(I) = (S + B)^{1/2}$ where S is the scan count and B equals $4(b_1 + b_2)$. Of the 3547 measured reflections, 1587 with $I > 3\sigma(I)$ were used in the final refinement of the structure parameters.

Solution and Refinement of the Structure. An estimate of the overall scale factor was obtained using Wilson's method and fractional coordinates for the two unique nickel atoms of the structure readily obtained from a sharpened three-dimensional Patterson map. A Fourier synthesis based on these nickel phases revealed a structural model which included all 32 nonhydrogen atoms. Using isotropic temperature factors and unit weights, full-matrix least-squares refinement of this model gave $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ a value of 0.078. The scattering functions of Cromer and Mann[24] were used for all nonhydrogen atoms treated as neutral species and the curve for the nickel atom was corrected for the real and imaginary part of the anomalous dispersion.[25] Two further cycles of refinement with anisotropic thermal parameters for all atoms reduced $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, the function minimized, to 0.059, at which point $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.055. The weighting scheme employed was $w^{1/2} = 1/[\sigma^2(F) + pF^2]^{1/2}$ with p = 0.0005, a factor introduced to avoid overweighting strong reflections;[26] this appears satisfactory in that the average values of the minimized function are independent of $|F_o|$.

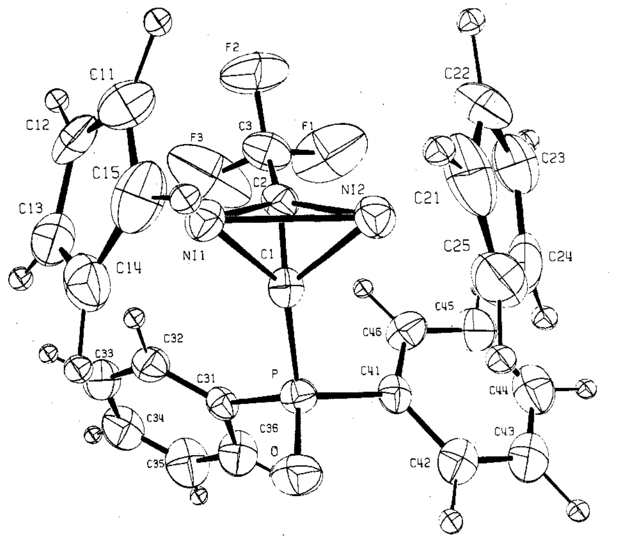

Figure 1. Perspective view with 50% probability ellipsoids of $[Ni(\eta^5\text{-}C_5H_5)]_2\text{-}\mu\text{-}(Ph_2P(O)C{\equiv}CCF_3)$ showing the molecular geometry and atomic numbering.

The top peaks of a difference Fourier map established positions for all of the hydrogen atoms; these were then allowed for (in chemically expected positions with isotropic U values of 0.063 Å^2 and scattering factors from ref 27) but not refined in subsequent calculations. Refinement of this model converged in two more cycles with R_1 = 0.040 and R_2 = 0.045 when the largest shift per error ratio was 0.55 for the z coordinate of the cyclopentadienyl carbon atom C(24). The error in an observation of unit weight is 1.13 and a final difference Fourier showed no significant features. Two strong, low-order reflections which seemed to be affected by secondary extinction were omitted from the final cycles of refinement. A listing of observed and calculated structure factors is available.[28]

Final positional and thermal parameters for the nonhydrogen atoms, along with their standard deviations as estimated from the inverse matrix, are listed in Table I. The calculated positions of the hydrogen atoms, with numbering corresponding to the attached carbon atom, are in Table II.

Description of the Structure

A view of the molecule together with the numbering scheme used throughout the discussion is shown in Figure 1. The structure consists of well-separated molecules of $[(\eta^5\text{-}C_5H_5)Ni]_2(Ph_2P(O)C_2CF_3)$. Figure 2 is an ORTEP[29] illustration of the unit cell contents. There are no abnormally short intermolecular contacts which justify comment. Interatomic distances and angles with their estimated standard deviations included in parentheses are shown in Table III.

Each nickel atom in the binuclear molecule is coordinated to a η^5-cyclopentadienyl group, two carbon atoms of the alkyne, and another nickel atom. The two central carbon atoms of the acetylenic ligand lie perpendicular to the two nickel atoms such that these four atoms form a quasi-tetrahedral unit. The Ni_2C_2 fragment possesses an approximate mirror plane (C_s symmetry) which passes through the C(1)–C(2) acetylenic bond and the midpoint of the Ni–Ni bond. The relative orientation of the two phenyl rings, which minimize H···H interactions, destroys the idealized C_s-m symmetry for the whole molecule. The coordination stereochemistry of each nickel atom is distorted tetrahedral if the η^5-C_5H_5 group is considered to occupy only one coordination position or distorted octahedral if the more usual definition of η^5-C_5H_5 as a tridentate ligand is used. The η^5-C_5H_5 ligands are essentially symmetrically bonded to nickel with the Ni–C(ring) bond

Table I. Final Positional[a] and Thermal[b] Parameters for $[Ni(\eta^5\text{-}C_5H_5)]_2\text{-}\mu\text{-}(Ph_2P(O)C{\equiv}CCF_3)$

Atom	*x*	*y*	*z*
Ni(1)	0.122 30 (3)	0.087 08 (7)	0.249 15 (5)
Ni(2)	0.089 67 (3)	0.181 74 (8)	0.132 59 (4)
P	0.096 14 (6)	0.409 04 (16)	0.266 66 (9)
F(1)	0.218 9 (2)	0.298 7 (6)	0.100 1 (4)
F(2)	0.231 3 (2)	0.107 1 (5)	0.127 0 (3)
F(3)	0.243 3 (2)	0.243 9 (8)	0.214 4 (4)
O	0.044 5 (2)	0.392 9 (4)	0.305 3 (3)
C(1)	0.119 1 (2)	0.265 7 (6)	0.222 2 (3)
C(2)	0.156 4 (2)	0.201 3 (6)	0.181 0 (3)
C(3)	0.212 1 (3)	0.211 9 (8)	0.157 0 (4)
C(11)	0.129 0 (3)	−0.114 1 (6)	0.249 9 (5)
C(12)	0.168 0 (3)	−0.060 2 (7)	0.298 8 (5)
C(13)	0.142 5 (3)	0.008 5 (7)	0.359 0 (4)
C(14)	0.087 5 (3)	−0.002 4 (7)	0.348 2 (4)
C(15)	0.078 6 (3)	−0.076 1 (7)	0.280 9 (5)
C(21)	0.030 1 (4)	0.073 8 (9)	0.080 5 (5)
C(22)	0.071 0 (3)	0.088 4 (9)	0.027 4 (4)
C(23)	0.077 6 (3)	0.218 9 (8)	0.013 1 (4)
C(24)	0.040 2 (4)	0.284 4 (7)	0.058 2 (5)
C(25)	0.010 3 (3)	0.195 2 (12)	0.099 6 (4)
C(31)	0.146 9 (3)	0.462 0 (6)	0.333 9 (3)
C(32)	0.180 5 (3)	0.377 5 (6)	0.371 0 (4)
C(33)	0.215 2 (3)	0.421 1 (8)	0.429 0 (4)
C(34)	0.216 2 (3)	0.548 8 (9)	0.447 7 (5)
C(35)	0.183 6 (4)	0.634 1 (8)	0.410 0 (5)
C(36)	0.149 1 (3)	0.591 4 (7)	0.353 0 (4)
C(41)	0.094 1 (3)	0.526 2 (5)	0.189 3 (3)
C(42)	0.048 1 (3)	0.599 2 (6)	0.178 8 (4)
C(43)	0.044 2 (3)	0.685 7 (7)	0.117 5 (5)
C(44)	0.085 6 (4)	0.698 2 (7)	0.064 9 (4)
C(45)	0.132 1 (3)	0.627 1 (7)	0.075 2 (4)
C(46)	0.136 5 (2)	0.543 1 (6)	0.138 0 (4)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	3.28 (6)	2.56 (6)	3.56 (6)	0.06 (4)	−0.44 (4)	0.13 (4)
Ni(2)	3.46 (6)	3.25 (6)	3.05 (6)	−0.17 (4)	−0.46 (4)	−0.19 (4)
P	2.86 (10)	2.69 (10)	3.18 (10)	0.04 (8)	0.25 (7)	0.01 (8)
F(1)	9.0 (4)	9.7 (4)	17.0 (6)	0.6 (3)	8.3 (4)	4.7 (4)
F(2)	5.1 (3)	8.6 (4)	11.8 (4)	1.8 (3)	2.3 (3)	−3.1 (3)
F(3)	4.3 (3)	26.9 (9)	11.8 (4)	−5.2 (4)	1.0 (3)	−9.8 (5)
O	3.5 (3)	4.6 (3)	5.0 (3)	0.3 (2)	1.0 (2)	−0.2 (2)
C(1)	3.3 (4)	3.2 (4)	2.8 (3)	−0.1 (3)	−0.3 (3)	0.3 (3)
C(2)	3.4 (4)	2.9 (4)	2.8 (3)	−0.4 (3)	−0.1 (3)	−0.4 (3)
C(3)	4.5 (5)	5.6 (6)	5.1 (5)	−0.8 (4)	1.4 (4)	−1.0 (4)
C(11)	8.2 (6)	2.2 (4)	5.9 (4)	0.3 (4)	−0.1 (5)	−0.0 (4)
C(12)	4.7 (4)	3.5 (4)	6.9 (5)	2.0 (4)	−0.7 (4)	1.5 (4)
C(13)	5.5 (5)	4.1 (4)	4.7 (4)	0.3 (4)	−1.2 (4)	0.8 (4)
C(14)	5.7 (5)	4.4 (4)	3.6 (4)	−0.5 (4)	0.3 (4)	1.1 (4)
C(15)	5.3 (5)	3.7 (4)	6.9 (5)	−1.0 (4)	−0.6 (4)	1.9 (4)
C(21)	7.2 (6)	7.2 (6)	4.6 (5)	−3.5 (5)	−2.6 (4)	0.3 (5)
C(22)	7.4 (6)	6.9 (6)	4.1 (4)	0.7 (5)	−0.5 (4)	−2.4 (5)
C(23)	6.9 (5)	6.9 (6)	3.5 (4)	−0.7 (4)	−0.5 (4)	1.1 (4)
C(24)	9.5 (7)	4.8 (5)	5.9 (5)	2.0 (5)	−5.2 (4)	−0.7 (4)
C(25)	3.7 (4)	13.3 (9)	4.2 (4)	1.1 (5)	−0.1 (3)	−1.6 (6)
C(31)	3.9 (4)	2.7 (3)	2.8 (3)	−0.4 (3)	0.0 (3)	−0.2 (3)
C(32)	4.8 (4)	4.4 (4)	4.1 (4)	0.3 (3)	−0.3 (4)	−0.6 (3)
C(33)	4.7 (4)	6.6 (6)	4.9 (4)	0.3 (4)	−1.3 (4)	−0.6 (4)
C(34)	6.3 (5)	7.1 (6)	5.3 (5)	−1.4 (5)	−1.4 (4)	−2.0 (5)
C(35)	9.3 (7)	4.5 (5)	6.6 (6)	−1.7 (5)	−1.4 (5)	−1.5 (4)
C(36)	6.9 (5)	4.2 (5)	5.7 (5)	−0.3 (4)	−1.4 (4)	−0.5 (4)
C(41)	4.0 (4)	2.5 (3)	3.4 (3)	−0.5 (3)	−0.8 (3)	−0.2 (3)
C(42)	4.2 (4)	3.4 (4)	5.3 (4)	−0.4 (4)	−1.1 (3)	−0.1 (4)
C(43)	5.8 (5)	4.5 (4)	6.1 (5)	0.1 (4)	−1.8 (4)	0.1 (4)
C(44)	8.9 (6)	3.4 (4)	5.5 (5)	−0.0 (4)	−1.4 (5)	0.9 (4)
C(45)	7.4 (6)	4.7 (5)	5.4 (5)	0.2 (4)	1.4 (4)	1.8 (4)
C(46)	4.1 (4)	4.0 (4)	5.8 (4)	0.3 (3)	0.8 (4)	1.1 (4)

[a] The estimated standard deviations of the last digit are in parentheses. [b] The thermal parameters U_{ij} (Å^2 × 10^2) are terms in the expression: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

lengths ranging between 2.099 (7) and 2.118 (7) Å for Ni(1) and between 2.078 (9) and 2.093 (7) Å for Ni(2). Comparable distances have been found in $[(\eta^5\text{-}C_5H_5)Ni]_2(CNMe)_2$[30] [mean 2.13 Å] and $[(\eta^5\text{-}C_5H_5)Ni]_2(Ph_2C_2)$[11] [mean 2.11 Å].

The main structural features of interest are the metal–acetylene bonding and the geometry of the coordinated acetylenic phosphine oxide. Nickel–carbon bond lengths within the Ni_2C_2 cluster show some interesting variations in length which may reflect the inherent asymmetry of the alkyne and the electronegativity of the attached groups. Thus, the individual Ni–C(2) distances [Ni(1)–C(2) = 1.873 (6) Å and Ni(2)–C(2) = 1.889 (6) Å] differ significantly from the

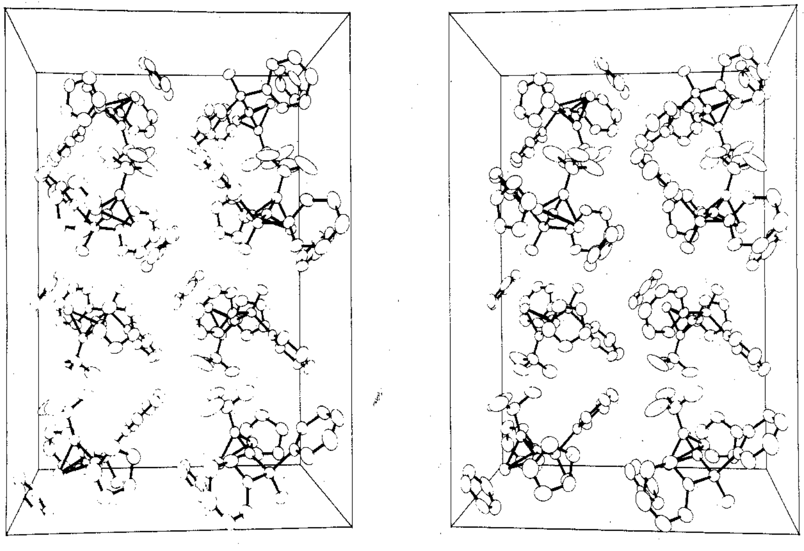

Figure 2. Stereoview of the molecular packing diagram of $[Ni(\eta^5\text{-}C_5H_5)]_2\text{-}\mu\text{-}(Ph_2P(O)C{\equiv}CCF_3)$. The hydrogen atoms have been omitted for clarity.

Table II. Positional Parameters for the Hydrogen Atoms of $[Ni(\eta^5\text{-}C_5H_5)]_2\text{-}\mu\text{-}(Ph_2P(O)C{\equiv}CCF_3)$

Atom	*x*	*y*	*z*
H(11)	0.137	−0.171	0.198
H(12)	0.210	−0.070	0.295
H(13)	0.161	0.062	0.405
H(14)	0.056	0.037	0.385
H(15)	0.041	−0.104	0.256
H(21)	0.015	−0.016	0.103
H(22)	0.093	0.011	0.001
H(23)	0.106	0.265	−0.024
H(24)	0.035	0.386	0.061
H(25)	−0.023	0.212	0.138
H(32)	0.181	0.277	0.355
H(33)	0.240	0.356	0.461
H(34)	0.244	0.587	0.489
H(35)	0.185	0.733	0.425
H(36)	0.124	0.659	0.324
H(42)	0.015	0.585	0.218
H(43)	0.010	0.743	0.110
H(44)	0.080	0.762	0.016
H(45)	0.164	0.640	0.035
H(46)	0.172	0.492	0.147

Ni–C(1) lengths [Ni(1)–C(1) = 1.920 (6) Å and Ni(2)–C(1) = 1.909 (6) Å]. It is tempting to suggest that the shorter bonds to the alkyne atom bearing a trifluoromethyl substituent result from greater polarization of dπ(Ni)–pπ*(alkyne) bonding electrons toward this atom. This opinion is reinforced by the relative magnitudes of the angles C(1)–C(2)–C(3) [140.7 (6)°] and P–C(1)–C(2) [150.2 (5)°] in the now familiar cis-bent geometry of the coordinated alkyne [C≡C = 1.353 (9) Å]. The alternative explanation is that asymmetry in the nickel–alkyne bonding results from the greater steric bulk of the oxodiphenylphosphino moiety compared with that of the CF_3 group. However, the absence of significant intramolecular interactions between the phenyl and cyclopentadienyl groups does not support this latter argument. The Ni–Ni bond distance [2.365 (1) Å] is significantly longer than in $[(\eta^5\text{-}C_5H_5)Ni]_2(Ph_2C_2)$ [2.329 (4) Å][11] and $[\eta^5\text{-}C_5H_5)\text{-}Ni]_2(CNMe)_2$ [2.322 (1) Å][30] but is still at the lower end of the range of values for dinickel complexes.[10] Further data on Ni–Ni bond lengths in alkyne-bridged complexes will be necessary before any relationship between Ni–C and Ni–Ni bond lengths and the stereochemistry of the Ni_2C_2 cluster can be definitely established. It is interesting to note that Cotton and co-workers[31] have reported an analogous cobalt structure, $((t\text{-}Bu)_2C_2)Co_2(CO)_6$, and quoted a Co—Co single bond of 2.463 (1) Å, four equivalent Co—C bonds, 1.995–2.003 (4) Å, and an acetylenic C≡C bond of 1.335 (6) Å. The C≡C bond distances for the bridged acetylide groups in related compounds (see Table IV) are all essentially similar.

The cis-bent alkyne ligand has a fully staggered conformation about the C(2)–C(3) and P–C(1) bonds as shown clearly in Figure 1 and established by the dihedral angles O–P–C(1)–C(2) [−179.4 (9)°] and C(1)–C(2)–C(3)–F(2) [168.7 (8)°].

Comment has been made previously[32] on the apparent shortening of P—C(sp) bond lengths in the phosphinoalkyne complex $Pt(NCS)(SCN)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$[32] where only the phosphorus atom is coordinated and this has been attributed to the presence of dπ(P)–pπ(C) interactions. More recently, ^{31}P and ^{13}C NMR shift data have been interpreted as indicating appreciable contributions from resonance forms of the type $R_3P{=}C{=}C^+R'X^-$ in alkylphosphonium salts.[33] For $[(\eta^5\text{-}C_5H_5)Ni]_2(Ph_2P(O)C_2CF_3)$ the alkyne π orbitals are employed in bonding to the two nickel atoms and the phosphorus atom is multiply bonded to an oxygen atom. Hence, multiple bonding of the type dπ(P)–pπ(C), would be precluded. Consistent with this is the observed P—C(alkyne) distance (1.774 (6) Å) which is 0.07 (3) Å longer than the P—C(alkyne) distance (1.70 (3) Å) in *cis*-Pt(NCS)-$(SCN)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$.[32] The P—C(1) bond length in the present complex is shorter by 0.028 (8) Å than the average of the P—C(31) and P—C(41) bond lengths in accord with the expected differences arising from the sp and sp^2 hybridization at C(1) and at C(31), C(41), respectively.

The phosphorus–oxygen bond distance [1.473 (5) Å] appears to be normal for a phosphine oxide.[34,35] The O–P–C angles [mean 112.5 (2)°] are large when compared with the C–P–C angles [mean 106.3 (8)°], illustrating, presumably, the effects of nonbonded pair–bonded pair and double bonded pair–bonded pair repulsions on molecular stereochemistry. The C–C–F angles [mean 113.0 (7)°] are larger than the F–C–F angles 105.8 (18)°, presumably reflecting the greater steric requirements of the Ni_2C_2 moiety.

The cyclopentadienyl and phenyl rings have normal geometry with mean carbon–carbon distances of 1.402 (14) and 1.386 (11) Å, respectively, and mean C–C–C angles of 108.0 (6) and 120.0 (5)°, respectively.

The formation of $[(\eta^5\text{-}C_5H_5)Ni]_2(Ph_2P(O)C_2CF_3)$ probably involves an intermediate phosphine complex $[(\eta^5\text{-}C_5H_5)\text{-}Ni]_2(Ph_2PC_2CF_3)$ analogous to $[(\eta^5\text{-}C_5H_5)Ni]_2(Ph_2PC_2\text{-}t\text{-}Bu)$.[17] The formation of a phosphine oxide complex $[(\eta^5\text{-}$

$C_5H_5)Ni]_2(Ph_2P(O)C_2$-*t*-Bu) from the latter involved an oxidation on the alumina column during chromatography. A similar but more rapid column oxidation almost certainly accounts for the formation of the present complex $[(\eta^5$-$C_5H_5)Ni]_2(Ph_2P(O)C_2CF_3)$. Finally, $[(\eta^5$-$C_5H_5)Ni]_2(Ph_2P(O)C_2CF_3)$ reacts further with excess $Ph_2PC\equiv CCF_3$ generating a complex $[(\eta^5$-$C_5H_5)Ni]_2(Ph_2P(O)C_2CF_3)(Ph_2PC_2CF_3)$ whose characterization will be described separately.[15]

Table III. Interatomic Distances (Å) and Angles (deg) for $[Ni(\eta^5$-$C_5H_5)]_2$-μ-$(Ph_2P(O)C\equiv CCF_3)$

(a) Distances

Ni(1)–Ni(2)	2.365 (1)	C(1)–C(2)	1.353 (9)
Ni(1)–C(1)	1.920 (6)	C(2)–C(3)	1.472 (10)
Ni(2)–C(1)	1.909 (6)	C(11)–C(12)	1.407 (11)
Ni(1)–C(2)	1.873 (6)	C(12)–C(13)	1.406 (11)
Ni(2)–C(2)	1.889 (6)	C(13)–C(14)	1.406 (11)
Ni(1)–C(11)	2.104 (6)	C(14)–C(15)	1.397 (10)
Ni(1)–C(12)	2.100 (7)	C(11)–C(15)	1.436 (11)
Ni(1)–C(13)	2.104 (7)	C(21)–C(22)	1.383 (12)
Ni(1)–C(14)	2.118 (7)	C(22)–C(23)	1.392 (12)
Ni(1)–C(15)	2.099 (7)	C(23)–C(24)	1.398 (12)
Ni(2)–C(21)	2.078 (9)	C(24)–C(25)	1.390 (13)
Ni(2)–C(22)	2.092 (8)	C(21)–C(25)	1.400 (15)
Ni(3)–C(23)	2.093 (7)	C(31)–C(32)	1.378 (9)
Ni(4)–C(24)	2.078 (9)	C(32)–C(33)	1.396 (10)
Ni(5)–C(25)	2.089 (7)	C(33)–C(34)	1.369 (12)
P–O	1.473 (5)	C(34)–C(35)	1.372 (12)
		C(35)–C(36)	1.378 (12)
P–C(31)	1.807 (6)	C(31)–C(36)	1.389 (10)
P–C(41)	1.797 (6)	C(41)–C(42)	1.401 (9)
P–C(1)	1.774 (6)	C(42)–C(43)	1.381 (10)
C(3)–F(1)	1.336 (10)	C(43)–C(44)	1.385 (11)
C(3)–F(2)	1.300 (10)	C(44)–C(45)	1.401 (12)
C(3)–F(3)	1.298 (10)	C(45)–C(46)	1.386 (10)
		C(41)–C(46)	1.395 (9)

(b) Angles

Ni(1)–C(1)–Ni(2)	76.3 (2)	C(11)–C(12)–C(13)	108.3 (7)
Ni(1)–C(2)–Ni(2)	77.9 (2)	C(12)–C(13)–C(14)	108.5 (6)
P–C(1)–C(2)	150.2 (5)	C(13)–C(14)–C(15)	108.1 (6)
C(1)–C(2)–C(3)	140.7 (6)	C(14)–C(15)–C(11)	108.1 (7)
		C(15)–C(11)–C(12)	107.1 (7)
Ni(1)–C(1)–P	136.8 (3)	C(21)–C(22)–C(23)	108.2 (8)
Ni(2)–C(1)–P	126.8 (3)	C(22)–C(23)–C(24)	107.5 (7)
Ni(1)–C(2)–C(3)	131.3 (5)	C(23)–C(24)–C(25)	108.7 (8)
Ni(2)–C(2)–C(3)	138.0 (5)	C(24)–C(25)–C(21)	107.1 (7)
C(2)–C(3)–F(1)	112.0 (6)	C(25)–C(21)–C(22)	108.6 (8)
C(2)–C(3)–F(2)	113.8 (6)	C(31)–C(32)–C(33)	120.2 (6)
C(2)–C(3)–F(3)	113.1 (6)	C(32)–C(33)–C(34)	119.5 (7)
F(1)–C(3)–F(2)	103.7 (6)	C(33)–C(34)–C(35)	120.7 (7)
F(1)–C(3)–F(3)	107.0 (7)	C(34)–C(35)–C(36)	120.0 (7)
F(2)–C(3)–F(3)	106.6 (7)	C(35)–C(36)–C(31)	120.2 (7)
O–P–C(1)	112.7 (3)	C(36)–C(31)–C(32)	119.3 (6)
O–P–C(31)	112.4 (3)	C(41)–C(42)–C(43)	120.7 (6)
O–P–C(41)	112.3 (3)	C(42)–C(43)–C(44)	119.7 (7)
C(1)–P–C(31)	107.2 (3)	C(43)–C(44)–C(45)	120.3 (7)
C(1)–P–C(41)	105.6 (3)	C(44)–C(45)–C(46)	119.9 (7)
C(31)–P–C(41)	106.1 (3)	C(45)–C(46)–C(41)	120.0 (6)
		C(46)–C(41)–C(42)	119.3 (6)

Table IV. Bridged Metal-Metal Bond Distances in Nickel and the Corresponding Cobalt Complexes

Compd	M–M, Å	C≡C, Å	Ref
$[(\eta^5$-$C_5H_5)Ni]_2(Ph_2P(O)C_2CF_3)$	2.365 (1)	1.353 (9)	This work
$[(\eta^5$-$C_5H_5)Ni]_2(C_2H_2)$	2.345 (3)	1.341 (6)	36[a]
$[(\eta^5$-$C_5H_5)Ni]_2(CNMe)_2$	2.322 (1)		30[b]
$[(\eta^5$-$C_5H_5)Ni]_2(Ph_2C_2)$	2.329 (4)	1.35 (3)	11
$[(CO)_3Co]_2(Ph_2C_2)$	2.47	1.369	37[c]
$[(CO)_3Co]_2((t$-$Bu)_2C_2)$	2.463 (1)	1.335 (6)	31[d]

[a] Coppens and Wang have ascertained from electron density maps that this complex contains a "straight" rather than a "bent" nickel-nickel bond. [b] This complex contains bridging methyl isocyanide groups. Cotton and co-workers have estimated a value in the range 2.32–2.36 Å for a single nickel-nickel bond when bridged in a sterically favorable fashion. [c] This complex is isoelectronic with the preceding compound. [d] The closely related complex $[(CO)_3Fe]_2((t$-$Bu)_2C_2)$ has been reported by the same authors to contain an Fe–Fe double bond of 2.316 (1) Å and C≡C bond length of 1.311 (10) Å.

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Registry No. $[Ni(\eta^5$-$C_5H_5)]_2$-μ-$(Ph_2P(O)C\equiv CCF_3$, 60498-73-9; $(\eta^5$-$C_5H_5)_2Ni$, 1271-28-9.

Supplementary Material Available: Listing of structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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