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# REACTIONS OF TETRACYANOETHYLENE WITH TRANSITION-METAL ACETYLIDES: SYNTHESIS AND STRUCTURE OF $Rh(C{\equiv}CPh)[\eta^2\text{-}C_2(CN)_4](NCMe)(PPh_3)_2$

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## Summary

The title complex was obtained from the adduct of $C_2(CN)_4$ and $Rh(C{\equiv}CPh)(CO)(PPh_3)_2$ by simple substitution of CO in refluxing acetonitrile. Crystals of the complex are orthorhombic, with *a* 10.058(2), *b* 20.008(4), *c* 21.594(5) Å, space group $P2_12_12_1$, $Z = 4$. The rhodium has approximate trigonal bipyramidal coordination, with apical NCMe and $C_2Ph$ ligands: Rh—$C_2$Ph, 1.939(18); Rh—C(olefinic), 2.151, 2.157(19); Rh—N, 2.051(16); Rh—P, 2.377, 2.397(6) Å.

## Introduction

Recently we and others have described several aspects of the complex reactions that occur between transition metal acetylides, such as $W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)$ [1], $Fe(C{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$ [1,2], or $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ [3] and electron-deficient olefins, including $C_2(CN)_4$. In seeking to extend the scope of these reactions, we have studied those occurring between selected rhodium(I) and iridium(I) acetylides and tetracyanoethylene. Others have reported that tetracyanoethylene reacts with $Rh(C{\equiv}CR)(CO)(PPh_3)_2$ (R = Me or Et) to give the simple adducts, $Rh(C{\equiv}CR)[\eta^2\text{-}C_2(CN)_4](CO)(PPh_3)_2$ [4]; neither these nor the similar adduct from R=Ph showed any $\nu$(CC) band in the IR spectrum, so we considered the possibility that addition of the olefin to the C≡C triple bond had occurred. While attempting to obtain suitable crystals, we have found a new example of the replacement of CO by MeCN.

## Experimental

### *Reaction between $Rh(C{\equiv}CPh)(CO)(PPh_3)_2$ and tetracyanoethylene*

Solutions of $Rh(C{\equiv}CPh)(CO)(PPh_3)_2$ (420 mg, 0.56 mmol) and tetracyano-

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ethylene (80 mg, 0.63 mmol) in dichloromethane (20 ml) were mixed and allowed to react for 2 h. Evaporation and crystallisation from methanol gave yellow microcrystals of $Rh(C{\equiv}CPh)[\eta^2\text{-}C_2(CN)_4](CO)(PPh_3)_2 \cdot 0.025CH_2Cl_2$ (1) (470 mg, 94%), dec. >160°C (Found: C, 67.0; H, 4.0; N, 6.2; $C_{51}H_{35}N_4OP_2Rh \cdot 0.25CH_2Cl_2$ calcd.: C, 67.9; H, 4.0; N, 6.2%). Infrared ($CH_2Cl_2$): $\nu$(CN) 2229w, 2223w; $\nu$(CO) + $\nu$(CC) 2083s $cm^{-1}$; other bands at 1432m, 1427m, 1304vw, 1208vw, 1183vw, 1149vw, 1085(sh), 1080m, 1014vw, 991vw, 753vw, 743m, 737m, 711vw, 700w, 688m, 680(sh), 658 w $cm^{-1}$) (in Nujol). $^1$H NMR: $\delta$ ($CDCl_3$) 5.3, s, 0.5H, $CH_2Cl_2$; 7.4, m, 35H, Ph.

### *Reaction of* 1 *with acetonitrile*

A solution of complex 1 (90 mg, 0.1 mmol) was heated at reflux point in acetonitrile (20 ml) for 30 min; a bright yellow powder of $Rh(C{\equiv}CPh)[\eta^2\text{-}C_2(CN)_4](NCMe)(PPh_3)_2$ (2) (78 mg, 85%), dec. >160°C, was precipitated (Found: C, 69.4; H, 4.8; N, 7.3; $C_{52}H_{38}N_5P_2Rh$ calcd.: C, 69.6; H, 4.3; N, 7.8%). Infrared ($CH_2Cl_2$): $\nu$(CN) 2226m, 2137m; $\nu$(CC) 2073vw; other bands at 1588w, 1433m, 1307vw, 1197w, 1187vw, 1178(sh), 1149vw, 1085(sh), 1081m, 1019vw, 991w, 750m, 739m, 734(sh), 688s, 658w $cm^{-1}$ (Nujol). $^1$H NMR: $\delta$ ($CDCl_3$) 1.80, s, 3H, Me; 7.6, m, 30H, Ph; $^{13}$C NMR: $\delta$ ($CDCl_3$) 63.0, s, Me; 125.6—134.9, m, Ph.

### *Crystal structure determination*

The crystals of 2 form fine yellow needles, elongated in the *a* direction. A sample (0.02 × 0.06 × 0.19 mm) was mounted on a glass fibre with epoxy resin. Precession photography, employed in the preliminary studies, indicated an orthorhombic space group.

Lattice parameters were determined at 23°C from 25 independent reflections, measured and refined by scans performed on an Enraf-Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo-$K_\alpha$ radiation, by a least-squares fit to the setting parameters.

*Crystal data.* $C_{52}H_{38}N_5P_2Rh$, $M$ 897.7, orthorhombic, space group $P2_12_12_1$; $a$ 10.058(2), $b$ 20.008(4), $c$ 21.594(5) Å; $D_c$ 1.372, $D_m$ 1.37(2) g $cm^{-1}$; $U$ 4345.4 Å$^3$, $Z$ 4; $\mu$(Mo-$K_\alpha$) 4.67 $cm^{-1}$, $\lambda$(Mo-$K_\alpha$) 0.7107 Å, $F$(000) 1840 electrons.

Intensity data were collected in the range $1.5 < \theta < 22.5°$ using an $(\omega - \frac{n}{3}\theta)$ scan where $n$, optimized by peak analysis, was 4. The $\omega$ scan angles and horizontal counter apertures employed were $(1.00 + 0.33 \tan\theta)°$ and $(2.40 + 0.50 \tan\theta)$ mm respectively. Data reduction and correction for Lorentz and polarization effects was performed using programme SUSCAD [5]. Correction for absorption was not made because of the low absorption coefficient. Of the 2540 reflections collected, 1135 with $I > 2.5\,\sigma(I)$ were accepted and used in the calculations.

*Structure solution and refinement.* The position of the rhodium atom was determined from a three-dimensional Patterson synthesis and solution then proceeded via normal heavy atom techniques, all other non-hydrogen atoms being located from subsequent difference Fourier maps phased on the rhodium metal atom. All phenyl groups were included as rigid planar groups (C—C 1.380 Å). The protons of the phenyl and methyl groups were included at calculated sites

*(continued on p. 109)*

TABLE 1

POSITIONAL ($\times10^4$) AND THERMAL ($\times10^3$) PARAMETERS FOR $Rh(C{\equiv}CPh)[\eta^2\text{-}C_2(CN)_4](NCMe)(PPh_3)_2$

| | $x$ | $y$ | $z$ | $U_{11}$ |
|---|---|---|---|---|
| Rh | 4287(2) | −269(1) | 7235(1) | 24(1) |
| P(1) | 2630(5) | 406(2) | 7730(3) | 32(3) |
| C(1) | 341(12) | 1073(5) | 7317(5) | 45(6) |
| C(2) | −321(12) | 1577(5) | 7009(5) | 41(6) |
| C(3) | 390(12) | 2070(5) | 6709(5) | 37(6) |
| C(4) | 1761(12) | 2059(5) | 6718(5) | 57(8) |
| C(5) | 2423(12) | 1555(5) | 7026(5) | 43(6) |
| C(6) | 1712(12) | 1062(5) | 7326(5) | 28(5) |
| C(7) | 3450(14) | 1541(6) | 8433(6) | 52(7) |
| C(8) | 4009(14) | 1842(6) | 8946(6) | 59(8) |
| C(9) | 4480(14) | 1456(6) | 9428(6) | 83(9) |
| C(10) | 4393(14) | 769(6) | 9397(6) | 51(6) |
| C(11) | 3834(14) | 467(6) | 8885(6) | 37(6) |
| C(12) | 3363(14) | 853(6) | 8403(6) | 23(5) |
| C(13) | 806(13) | −634(6) | 7785(5) | 39(5) |
| C(14) | −207(13) | −1017(6) | 8030(5) | 53(7) |
| C(15) | −789(13) | −837(6) | 8584(5) | 56(7) |
| C(16) | −357(13) | −274(6) | 8894(5) | 65(7) |
| C(17) | 657(13) | 108(6) | 8650(5) | 45(6) |
| C(18) | 1239(13) | −72(6) | 8095(5) | 25(5) |
| P(2) | 3335(6) | −621(3) | 6281(3) | 33(4) |
| C(19) | 4570(16) | −969(8) | 5717(6) | 52(7) |
| C(20) | 4184(16) | −1467(8) | 5314(6) | 92(9) |
| C(21) | 5056(16) | −1694(8) | 4867(6) | 78(9) |
| C(22) | 6313(16) | −1422(8) | 4824(6) | 89(10) |
| C(23) | 6699(16) | −924(8) | 5227(6) | 86(10) |
| C(24) | 5827(16) | −697(8) | 5674(6) | 59(7) |
| C(25) | 1313(13) | 277(7) | 6002(5) | 38(6) |
| C(26) | 680(13) | 757(7) | 5651(5) | 36(5) |
| C(27) | 1255(13) | 982(7) | 5109(5) | 47(7) |
| C(28) | 2463(13) | 728(7) | 4919(5) | 58(7) |
| C(29) | 3096(13) | 248(7) | 5271(5) | 36(5) |
| C(30) | 2522(13) | 22(7) | 5812(5) | 33(6) |
| C(31) | 823(16) | −1283(6) | 6228(6) | 48(6) |
| C(32) | −5(16) | −1818(6) | 6344(6) | 73(9) |
| C(33) | 511(16) | −2406(6) | 6577(6) | 66(8) |
| C(34) | 1856(16) | −2457(6) | 6695(6) | 74(9) |
| C(35) | 2684(16) | −1922(6) | 6580(6) | 51(7) |
| C(36) | 2168(16) | −1335(6) | 6346(6) | 46(7) |
| N(1) | 3680(15) | −1107(8) | 7704(9) | 37(4) |
| C(37) | 3519(22) | −1565(12) | 7976(10) | 52(7) |
| C(38) | 3282(29) | −2181(14) | 8304(13) | 111(11) |
| C(39) | 5958(17) | −241(10) | 7856(9) | 36(5) |
| C(40) | 6314(19) | −614(9) | 7303(11) | 36(6) |
| C(41) | 6541(20) | 417(11) | 7936(9) | 44(7) |
| N(2) | 7052(19) | 908(11) | 8030(8) | 65(6) |
| C(42) | 5929(23) | −612(10) | 8425(10) | 42(6) |
| N(3) | 5800(22) | −982(9) | 8821(8) | 65(6) |
| C(43) | 6434(20) | −1304(11) | 7305(12) | 48(6) |
| N(4) | 6450(17) | −1889(8) | 7311(9) | 56(5) |
| C(44) | 7405(22) | −329(13) | 6889(10) | 49(6) |
| N(5) | 8191(18) | −98(9) | 6627(8) | 56(6) |
| C(45) | 4903(17) | 471(9) | 6731(9) | 24(6) |
| C(46) | 5285(20) | 885(11) | 6386(9) | 45(7) |
| C(47) | 4861(12) | 1795(8) | 5588(7) | 59(7) |
| C(48) | 5308(12) | 2184(8) | 5103(7) | 72(9) |

TABLE 1 (continued)

| | | | | |
|---|---|---|---|---|
| C(49) | 6579(12) | 2097(8) | 4876(7) | 70(8) |
| C(50) | 7404(12) | 1622(8) | 5135(7) | 70(8) |
| C(51) | 6957(12) | 1233(8) | 5620(7) | 74(9) |
| C(52) | 5685(12) | 1320(8) | 5847(7) | 33(5) |

*Other thermal parameters (X$10^3$) for heavy atoms*

| | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|
| Rh | 25(1) | 27(1) | 4(1) | 1(1) | 3(1) |
| P(1) | 27(4) | 25(3) | 7(4) | −4(4) | −2(3) |
| P(2) | 36(4) | 24(3) | −2(3) | −5(3) | 12(3) |

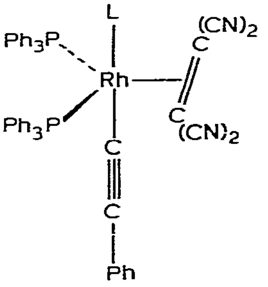
TABLE 2

HYDROGEN ATOM POSITIONAL (X$10^3$) AND THERMAL (X$10^2$) PARAMETERS FOR $Rh(C{\equiv}CPh)[\eta^2\text{-}C_2(CN)_4](NCMe)(PPh_3)_2$

| | $x$ | $y$ | $z$ | $U_{11}$ |
|---|---|---|---|---|
| H(1) | −15(1) | 73(1) | 752(1) | 11(2) |
| H(2) | −126(1) | 158(1) | 700(1) | 11(2) |
| H(3) | −7(1) | 242(1) | 650(1) | 11(2) |
| H(4) | 225(1) | 240(1) | 651(1) | 11(2) |
| H(5) | 337(1) | 155(1) | 703(1) | 11(2) |
| H(6) | 313(1) | 181(1) | 810(1) | 11(2) |
| H(7) | 407(1) | 232(1) | 897(1) | 11(2) |
| H(8) | 486(1) | 166(1) | 978(1) | 11(2) |
| H(9) | 472(1) | 50(1) | 973(1) | 11(2) |
| H(10) | 377(1) | −1(1) | 886(1) | 11(2) |
| H(11) | 121(1) | −76(1) | 740 | 11(2) |
| H(12) | −51(1) | −140(1) | 782 | 11(2) |
| H(13) | −149(1) | −110(1) | 875 | 11(2) |
| H(14) | −76(1) | −15(1) | 928 | 11(2) |
| H(15) | 96(1) | 50(1) | 886 | 11(2) |
| H(16) | 397(2) | −81(1) | 602(1) | 13(2) |
| H(17) | 332(2) | −165(1) | 534(1) | 13(2) |
| H(18) | 479(2) | −204(1) | 459(1) | 13(2) |
| H(19) | 691(2) | −158(1) | 452(1) | 13(2) |
| H(20) | 756(2) | −74(1) | 520(1) | 13(2) |
| H(21) | 92(1) | 12(1) | 637 | 13(2) |
| H(22) | −15(1) | 93(1) | 578 | 13(2) |
| H(23) | 82(1) | 131(1) | 487 | 13(2) |
| H(24) | 286(1) | 88(1) | 455 | 13(2) |
| H(25) | 393(1) | 7(1) | 514 | 13(2) |
| H(26) | 47(2) | −88(1) | 607(1) | 13(2) |
| H(27) | −93(2) | −178(1) | 626(1) | 13(2) |
| H(28) | −6(2) | −277(1) | 666(1) | 13(2) |
| H(29) | 221(2) | −286(1) | 686(1) | 13(2) |
| H(30) | 361(2) | −196(1) | 666(1) | 13(2) |
| H(31) | 392(3) | −224(1) | 862(1) | 7(4) |
| H(32) | 333(3) | −255(1) | 803(1) | 7(4) |
| H(33) | 242(3) | −216(1) | 848(1) | 7(4) |
| H(34) | 399(1) | 186(1) | 574(1) | 38(12) |
| H(35) | 474(1) | 251(1) | 492(1) | 38(12) |
| H(36) | 689(1) | 236(1) | 454(1) | 38(12) |
| H(37) | 828(1) | 156(1) | 498(1) | 38(12) |
| H(38) | 752(1) | 91(1) | 580(1) | 38(12) |

(C—H 0.95 Å) assuming planar and tetrahedral geometries, respectively.

Only rhodium and phosphorus atoms were refined anisotropically while the protons were assigned refined group temperature factors. Blocked-matrix least-squares techniques were employed throughout for the refinement of all positional and thermal parameters, an overall scale factor and an empirical isotropic extinction correction of the form $F_o = F_o(1 - 0.0001xF_o^2/\sin\theta)$, where $x$ refined to 0.00029. A weighting scheme was applied and refined, converging at $w = 1.03/(\sigma^2F_o + 0.001F_o^2)$, while overall refinement converged (all shifts $<0.1\sigma$) with $R = 0.047$ and $R_w = 0.047$. The structure was inverted, by changing the signs of all coordinates, and the final refinement sequence repeated, to give $R = 0.048$, $R_w = 0.048$, thus confirming the initially chosen absolute configuration at a confidence level of better than 99.5% [6]. A final difference map was structurally featureless with all peaks less than 0.4 e Å$^{-3}$. All calculations were performed using the SHELX system of programmes [7]. Positional and thermal parameters for the heavier atoms and the hydrogen atoms are given in Tables 1 and 2 respectively. Scattering factors (neutral Rh) were taken from International Tables [8]. Tables of calculated and observed structure factors are available (from M.I.B.) on request.



( 1 : L = CO ;
2 : L = MeCN )

## Results and discussion

As found with many other rhodium(I) complexes, tetracyanoethylene (tcne) adds to Rh(C≡CPh)(CO)(PPh$_3$)$_2$ to give the $\eta^2$-olefin complex **1**. No interaction of the electrophilic olefin with the acetylide group was found. In an attempt to promote an intramolecular reaction, we heated complex **1** in refluxing acetonitrile, when a second yellow complex formed, characterised as the acetonitrile complex **2** by physical methods, and by a single-crystal X-ray study.

The IR spectrum of **1** contains weak $\nu$(CN) bands at 2229 and 2223 cm$^{-1}$, together with a strong band at 2083 cm$^{-1}$, which contains overlapping $\nu$(CC) and $\nu$(CO) bands. In Rh(C≡CPh)(CO)(PPh$_3$)$_2$, $\nu$(CC) and $\nu$(CO) occur at 2094 and 1958 cm$^{-1}$, respectively; as expected, addition of the electrophilic olefin raises the $\nu$(CO) frequency by some 125 cm$^{-1}$.

The IR spectrum of complex **2** contains no strong band in the $\nu$(CO) region, although a weak absorption at 2073 cm$^{-1}$ remains; there are weak bands in the $\nu$(CN) regions: that at 2226 cm$^{-1}$ corresponds to those assigned to the tcne ligand in 1, while a band at 2137 $cm^{-1}$ suggests the presence of coordinated acetonitrile. This is supported by the microanalytical results and the NMR spectra. Although not unprecedented, substitution of CO by a nitrile is a surprising result, and we sought confirmation by a single cyrstal structure determination carried out on **2**.

*Description of structure*

The molecular structure of **2** is illustrated in Fig. 1 [9], which also gives the atom numbering scheme; Tables 3 and 4 list bond lengths and angles. The structure consists of discrete neutral complex molecules with no significant close contacts. Coordination about rhodium is approximately trigonal bipyramidal, with the two P atoms and the two olefinic C atoms (and hence the midpoint of the C(39)—C(40) bond) being coplanar. In contrast with $Rh(C{\equiv}CPh)(CO)(PPh_3)_2$, which is assumed to have mutually *trans* $PPh_3$ ligands, those in **2** are mutually *cis*; steric interactions between the three ligands in the trigonal plane has resulted in the P(1)—Rh—P(2) angle being considerably smaller (at 105.8(2)°) than the ideal trigonal value. The two apical coordination positions

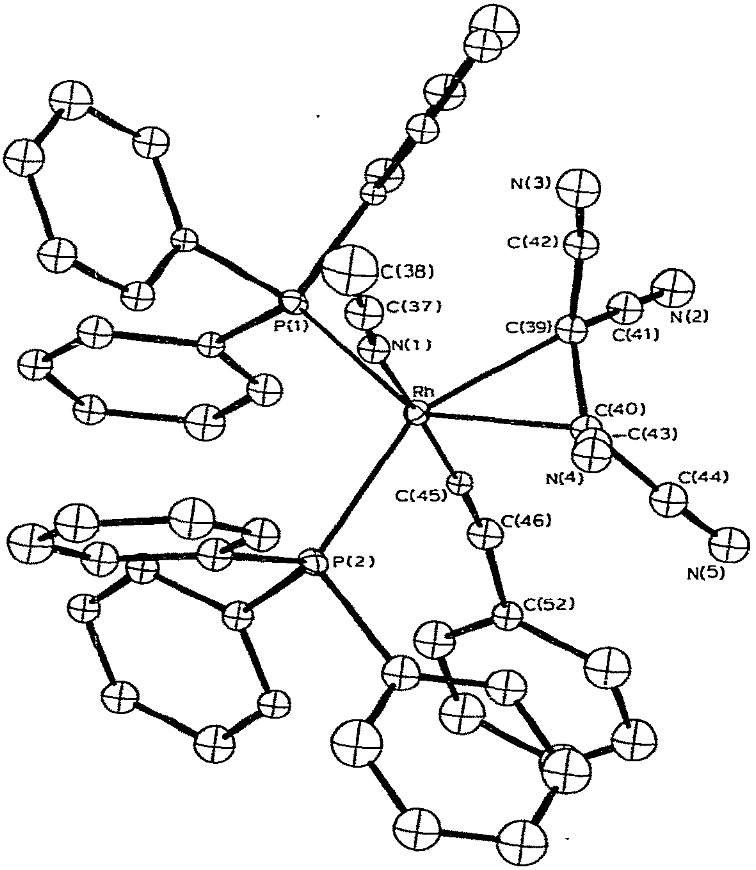


Fig. 1. The molecular structure of complex 2.

TABLE 3

BOND LENGTHS (Å) FOR $Rh(C{\equiv}CPh)[\eta^2\text{-}C_2(CN)_4](NCMe)(PPh_3)_2$

| | | | |
|---|---|---|---|
| P(1)—Rh | 2.397(5) | P(2)—Rh | 2.377(6) |
| N(1)—Rh | 2.051(16) | C(39)—Rh | 2.151(18) |
| C(40)—Rh | 2.157(19) | C(45)—Rh | 1.939(18) |
| C(6)—P(1) | 1.827(12) | C(12)—P(1) | 1.859(14) |
| C(18)—P(1) | 1.869(13) | C(19)—P(2) | 1.874(16) |
| C(30)—P(2) | 1.830(14) | C(36)—P(2) | 1.854(15) |
| C(37)—N(1) | 1.101(29) | C(38)—C(37) | 1.441(37) |
| C(40)—C(39) | 1.453(29) | C(41)—C(39) | 1.452(29) |
| C(42)—C(39) | 1.436(28) | C(43)—C(40) | 1.386(28) |
| C(44)—C(40) | 1.526(30) | N(2)—C(41) | 1.126(30) |
| N(3)—C(42) | 1.138(27) | N(4)—C(43) | 1.171(27) |
| N(5)—C(44) | 1.076(29) | C(46)—C(45) | 1.179(28) |
| C(52)—C(46) | 1.508(26) | | |

are occupied by the MeCN and C≡CPh ligands; the N(1)—Rh—C(45) angle is 174.9(7)°. The change in the geometry of tertiary phosphine coordination about the rhodium is a result of the presence of the cyanolefin ligand; there is less steric interaction of the latter with the cylindrical apical ligands than would result if the $PPh_3$ ligands were apical. The phenyl rings of the two $PPh_3$ ligands

TABLE 4

VALENCE ANGLES (DEGREES) FOR $Rh(C{\equiv}CPh)[\eta^2\text{-}C_2(CN)_4](NCMe)(PPh_3)_2$

| | | | |
|---|---|---|---|
| P(2)—Rh—P(1) | 105.8(2) | N(1)—Rh—P(1) | 91.9(5) |
| N(1)—Rh—P(2) | 93.8(5) | C(39)—Rh—P(1) | 104.5(5) |
| C(39)—Rh—P(2) | 149.6(5) | C(39)—Rh—N(1) | 86.9(7) |
| C(40)—Rh—P(1) | 143.8(6) | C(40)—Rh—P(2) | 110.2(6) |
| C(40)—Rh—N(1) | 89.3(7) | C(40)—Rh—C(39) | 39.4(8) |
| C(45)—Rh—P(1) | 92.4(5) | C(45)—Rh—P(2) | 82.4(6) |
| C(45)—Rh—N(1) | 174.9(7) | C(45)—Rh—C(39) | 94.6(7) |
| C(45)—Rh—C(40) | 88.9(7) | C(6)—P(1)—Rh | 122.9(5) |
| C(12)—P(1)—Rh | 110.2(5) | C(12)—P(1)—C(6) | 103.1(6) |
| C(18)—P(1)—Rh | 114.9(4) | C(18)—P(1)—C(6) | 101.0(6) |
| C(18)—P(1)—C(12) | 102.3(6) | C(1)—C(6)—P(1) | 121.5(9) |
| C(5)—C(6)—P(1) | 118.5(9) | C(7)—C(12)—P(1) | 122.9(10) |
| C(11)—C(12)—P(1) | 117.1(10) | C(13)—C(18)—P(1) | 116.6(9) |
| C(17)—C(18)—P(1) | 123.4(9) | C(19)—P(2)—Rh | 113.9(5) |
| C(30)—P(2)—Rh | 116.9(5) | C(30)—P(2)—C(19) | 101.4(6) |
| C(36)—P(2)—Rh | 114.7(5) | C(36)—P(2)—C(19) | 100.5(7) |
| C(36)—P(2)—C(30) | 107.5(7) | C(20)—C(19)—P(2) | 119.5(12) |
| C(24)—C(19)—P(2) | 120.3(11) | C(25)—C(30)—P(2) | 119.2(9) |
| C(29)—C(30)—P(2) | 120.8(10) | C(31)—C(36)—P(2) | 123.3(10) |
| C(35)—C(36)—P(2) | 116.5(12) | C(37)—N(1)—Rh | 171.0(17) |
| C(38)—C(37)—N(1) | 177.0(25) | C(40)—C(39)—Rh | 70.5(11) |
| C(41)—C(39)—Rh | 114.5(14) | C(41)—C(39)—C(40) | 117.7(17) |
| C(42)—C(39)—Rh | 120.2(14) | C(42)—C(39)—C(40) | 116.3(18) |
| C(42)—C(39)—C(41) | 112.0(17) | C(39)—C(40)—Rh | 70.1(10) |
| C(43)—C(40)—Rh | 113.6(14) | C(43)—C(40)—C(39) | 122.0(20) |
| C(44)—C(40)—Rh | 121.4(15) | C(44)—C(40)—C(39) | 117.8(17) |
| C(44)—C(40)—C(43) | 108.2(19) | N(2)—C(41)—C(39) | 175.0(22) |
| N(3)—C(42)—C(39) | 168.9(22) | N(4)—C(43)—C(40) | 175.8(22) |
| N(5)—C(44)—C(40) | 175.3(25) | C(46)—C(45)—Rh | 174.6(17) |
| C(52)—C(46)—C(45) | 168.7(21) | C(47)—C(52)—C(46) | 123.4(13) |
| C(51)—C(52)—C(46) | 116.6(14) | | |

mesh to accommodate these bulky (cone angle 145°) ligands *cis* to each other.

The olefinic $C{=}C$ bond has lengthened on coordination to 1.453(29) Å, which is within the range found for other $\eta^2$-$C_2(CN)_4$ complexes, e.g. 1.447(23) Å for $IrCl(CO)[\eta^2\text{-}C_2(CN)_4](AsPh_3)_2$ [10], 1.506(15) Å for $IrBr(CO)[\eta^2\text{-}C_2(CN)_4](PPh_3)_2$ [11], or 1.476(5) Å for $Ni[\eta^2\text{-}C_2(CN)_4](CNBu^t)_2$ [12]. The degree of bending back of the substituents can be described by the angles $\alpha$, $\beta$ and $\beta'$, as defined in reference 13, and in the present case, these have values of 69.5, 53.3 and 58.0° respectively. The Rh—C vectors are 2.151, 2.157(19) Å.

The phenylacetylide moiety is significantly bent at C(46) (angle C(45)—C(46)—C(52) is 168.7(21)°), but there is no lengthening of the $C{\equiv}C$ triple bond (1.179(28) Å) apparent. The Rh—C(*sp*) bond length is 1.939(18) Å, which is considerably shorter than that of 2.022(6) Å found in $RhAg_2(C_2C_6F_5)_5(PPh_3)_3$ [14]; since the latter is close to the sum of the covalent radii {1.32 [Rh(III)] + 0.69[C(*sp*)] = 2.01 Å}, this suggests that there is a degree of back-bonding from the metal into the phenylacetylide ligand in **2**. The Rh—N distance (2.051(16) Å) is somewhat longer than that of 1.98(2) Å found in $[Rh(\eta\text{-}C_2H_4)_3(NCMe)_2][BF_4]$ [15], and the Rh—P bonds 2.377, 2.397(6) Å fall within the range of previously reported distances.

This complex is apparently the first $Rh[\eta^2\text{-}C_2(CN)_4]$ species to be studied by X-ray diffraction, although no surprising features are revealed in the structure. It is not clear at present why cycloaddition of the cyanoolefinic to the metal acetylide residue does not occur in this case; no further reaction of **1** or **2** with excess tetracyanoethylene occurs. The substitution of CO by acetonitrile is unusual; the acetonitrile ligand in complex **2** is not particularly labile, in that substitution by other 2e donors does not occur readily.

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## References

1 M.I. Bruce, T.W. Hambley, J.R. Rodgers, M.R. Snow and A.G. Swincer, J. Organometal. Chem., 226 (1982) C1.
2 A. Davison and J.P. Solar, J. Organometal. Chem., 166 (1979) C13.
3 M.I. Bruce, J.R. Rodgers, M.R. Snow and A.G. Swincer, J. Chem. Soc., Chem. Commun., (1981) 271.
4 C.K. Brown, D. Georgiou and G. Wilkinson, J. Chem. Soc. (A), (1971) 3120.
5 SUSCAD — Data reduction programme for the CAD4 diffractometer, University of Sydney (1976).
6 W.C. Hamilton, Acta Crystallogr., 18 (1965) 502.
7 SHELX 76 — Programme for crystal structure determination, G.M. Sheldrick, University of Cambridge (1976).
8 International Tables for X-Ray Crystallography, volume IV, p. 99 (Kynoch Press, Birmingham 1974).
9 ORTEP — Thermal ellipsoid plotting; C.K. Johnson, (1965).
10 J.B.R. Dunn, R. Jacobs and C.J. Fritchie, J. Chem. Soc., Dalton Trans., (1972) 2007.
11 L. Manojlovic-Muir, K.W. Muir and J.A. Ibers, Disc. Faraday Soc., 47 (1969) 84.
12 J.K. Stalick and J.A. Ibers, J. Am. Chem. Soc., 92 (1970) 5333.
13 S.D. Ittel and J.A. Ibers, Adv. Organometal. Chem., 14 (1976) 33.
14 O.M. Abu Salah, M.I. Bruce, M.R. Churchill and B.G. DeBoer, J. Chem. Soc., Chem. Commun., (1974) 688; M.R. Churchill and B.G. DeBoer, Inorg. Chem., 14 (1975) 2630.
15 G. del Piero, G. Perego and M. Cesari, Cryst. Struct. Commun., 3 (1974) 15.