Organometallic complexes for nonlinear optics VI [1]: syntheses of rigid-rod ruthenium σ-acetylide complexes bearing strong acceptor ligands; X-ray crystal structures of trans-[Ru(C≡CC₆H₄NO₂-4)₂(dppm)₂] and trans-[Ru(C≡CC₆H₄C₆H₄NO₂-4,4')₂(dppm)₂]

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Abstract

A series of systematically-varied 'rigid-rod' octahedral ruthenium acetylide complexes, bearing the strong acceptor substituent $-NO_2$, of general formula $trans$-[Ru(C≡CC₆H₄R-4)₂(dppm)₂] (R = NO₂, C₆H₄NO₂-4, C₆H₄CH=CHC₆H₄NO₂-4, (E)) has been synthesized. X-ray structural studies of $trans$-[Ru(C≡CC₆H₄R-4)₂(dppm)₂] (R = NO₂, C₆H₄NO₂-4) confirm the $trans$-disposed geometry of the acetylide ligands and, for the latter, non-planarity of the biphenylene groups. The mixed acetylide 'rigid-rod' complex $trans$-[Ru(C≡CPh)(C≡CC₆H₄NO₂-4)(dppm)₂] has also been prepared. Semiempirical calculations employing ZINDO were performed on the mixed-acetylide complex, the results suggesting that the effect of $trans$-disposed ligands on the molecular quadratic hyperpolarizability β is not additive.

1. Introduction

The nonlinear optical responses of organometallic complexes have attracted a great deal of attention recently [2,3]. We [4] and others have utilized the experimentally simple Kurtz powder method [5] to evaluate bulk second-order responses, but results from such studies depend on a range of factors (molecular orientation in the crystal, linear optical effects, dispersion enhancement) which make attempts to extract structure–property information extremely difficult. Methods such as electric-field-induced second harmonic generation (EFISH) and hyper-Rayleigh scattering can afford molecular nonlinearities, but are experimentally de-

manding and rarely within the expertise of synthetic chemists. Attention has therefore recently turned to semiempirical methods as a predictor of molecular quadratic nonlinear optical responses; Kanis et al. have demonstrated that ZINDO, for example, accurately reproduces EFISH-derived nonlinearities for a range of main group and transition metal complexes [6–8]. We have been probing the optical nonlinearities of metal acetylide complexes [9,10], and have utilized ZINDO to extract structure–property information by examining a systematically-varied series of (cyclopentadienyl)ruthenium complexes; for these purposes relative rather than absolute values are sufficient.

Octahedral bis(acetylide) complexes of ruthenium have been extensively investigated recently [11–14] with all reported examples deriving from commercially available electron-donor acetylenes (HC≡CR; R = Ph, 'Bu, SiMe₃, H). We have been exploring the potential of

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[1] For Part V, see Ref. [1].
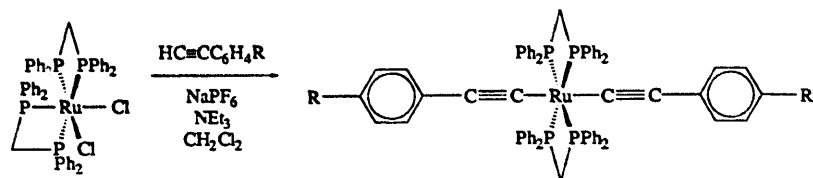
Scheme 1. R = –NO₂ (1) (62%), –C₆H₄NO₂-4 (2) (35%), –CH=CHC₆H₄NO₂-4, (E) (3) (16%).
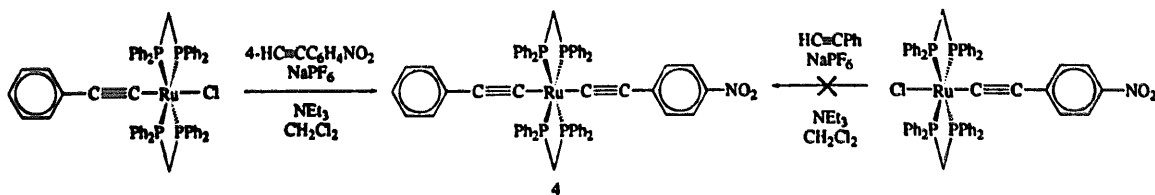
Scheme 2.

acetylenes incorporating the strong acceptor group $-NO_2$ for the syntheses of donor–acceptor metal acetylide complexes, which may have enhanced second-order nonlinear optical responses [1,9,10]. In addition, however, the extended conjugation present in octahedral bis(acetylide) ruthenium complexes could contribute to a heightened third-order nonlinear optical response. We

report herein the syntheses of some examples from this system, trans-[Ru(C≡CC₆H₄R-4)₂(dppm)₂] (R = NO₂, C₆H₄NO₂-4, CH=CHC₆H₄NO₂-4,(E)), and single crystal X-ray studies of the nitrophenyl- and nitro-biphenyl-acetylide complexes. The synthesis of the un-symmetrical bis(acetylide) complex trans-[Ru-(C≡CPh)(C≡CC₆H₄NO₂-4)(dppm)₂] is also reported,
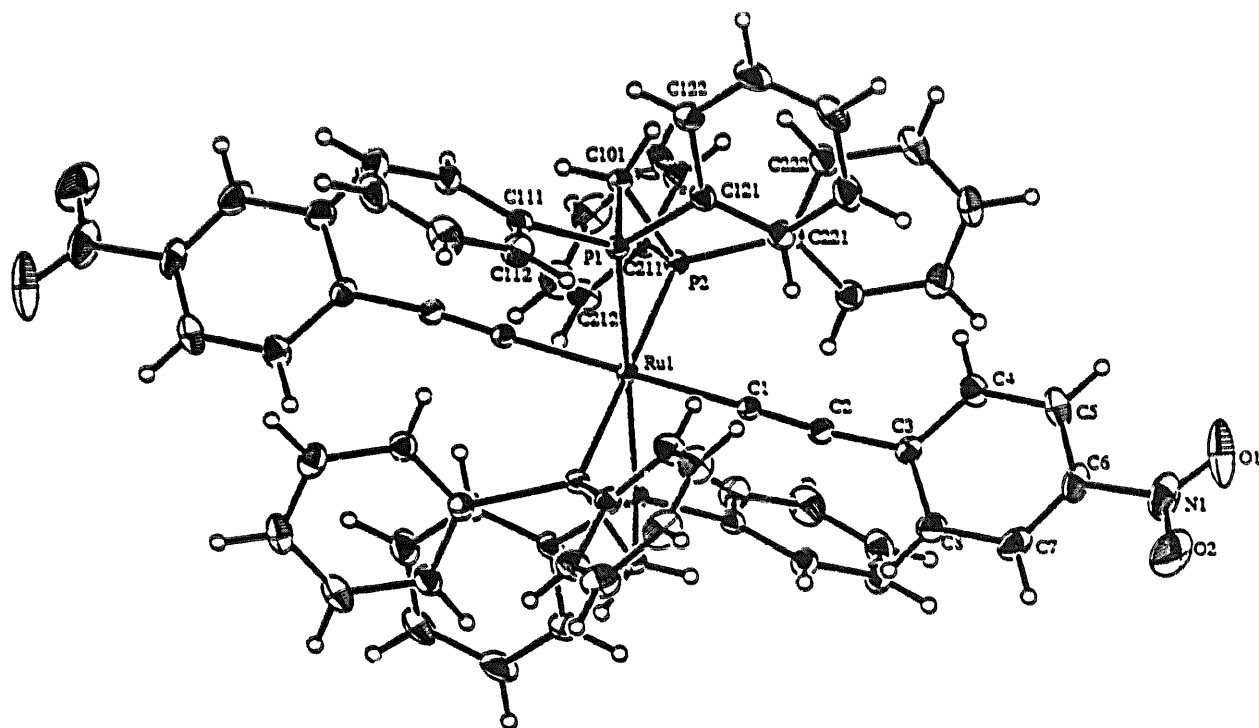
Fig. 1. Molecular geometry and atomic labelling scheme for trans-[Ru(C≡CC₆H₄NO₂-4)₂(dppm)₂] (1). 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms are drawn as circles of arbitrary radii.

together with semiempirical estimations of its second-order optical nonlinearity.

2. Results and discussion

2.1. Syntheses and characterization of the bis(acetylide) complexes

The symmetric complexes were prepared following the methodology in Scheme 1, analogous to that used by Dixneuf and coworkers [15]. The complexes were characterized by a combination of IR, ^{1}H, ^{13}C, and ^{31}P NMR, FAB MS, and satisfactory microanalyses. Thus, 1, 2 and 3 show characteristic $\nu(C\equiv C)$ at 2042 cm^{-1}, 2064 cm^{-1} and 2058 cm^{-1} respectively; the trend in

Table 1

Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms in trans-[Ru(C≡CC$_6$H$_4$NO$_2$-4)$_2$(dppm)$_2$] (1)

Atom	x	y	z	B_{eq}
Ru(1)	0.0000	0.0000	0.0000	2.233(8)
P(1)	0.26081(9)	−0.04311(7)	−0.10555(7)	2.63(2)
P(2)	0.11042(10)	0.12103(7)	0.04352(7)	2.60(2)
O(1)	−0.2541(8)	0.5692(4)	−0.5407(4)	12.5(2)
O(2)	−0.3497(6)	0.4519(5)	−0.5792(4)	10.2(2)
N(1)	−0.2885(6)	0.4845(5)	−0.5228(4)	7.6(1)
C(1)	−0.0818(4)	0.1126(3)	−0.1135(3)	2.62(7)
C(2)	−0.1335(4)	0.1784(3)	−0.1790(3)	3.13(8)
C(3)	−0.1787(4)	0.2578(3)	−0.2621(3)	3.15(8)
C(4)	−0.1070(5)	0.3436(3)	−0.3068(3)	4.06(10)
C(5)	−0.1480(6)	0.4194(3)	−0.3888(3)	4.9(1)
C(6)	−0.2560(5)	0.4080(4)	−0.4291(3)	5.0(1)
C(7)	−0.3295(5)	0.3266(5)	−0.3868(4)	5.5(1)
C(8)	−0.2918(5)	0.2526(4)	−0.3029(4)	4.7(1)
C(101)	0.3055(4)	0.0266(3)	−0.0085(3)	2.88(7)
C(111)	0.3761(4)	−0.1882(3)	−0.1193(3)	3.14(8)
C(112)	0.3833(5)	−0.2454(4)	−0.2074(4)	4.5(1)
C(113)	0.4629(6)	−0.3562(4)	−0.2203(4)	5.8(1)
C(114)	0.5382(6)	−0.4124(4)	−0.1456(5)	5.8(1)
C(115)	0.5308(5)	−0.3577(4)	−0.0579(4)	5.1(1)
C(116)	0.4510(4)	−0.2462(3)	−0.0446(3)	3.82(9)
C(121)	0.3514(4)	0.0198(3)	−0.2434(3)	3.12(8)
C(122)	0.5099(5)	−0.0073(4)	−0.2873(4)	4.45(10)
C(123)	0.5811(5)	0.0442(4)	−0.3869(4)	5.6(1)
C(124)	0.4957(6)	0.1234(4)	−0.4432(4)	5.5(1)
C(125)	0.3402(6)	0.1502(4)	−0.4013(4)	5.0(1)
C(126)	0.2671(4)	0.0982(3)	−0.3012(3)	3.93(9)
C(211)	0.0826(4)	0.1562(3)	0.1864(3)	3.12(8)
C(212)	−0.0046(5)	0.1038(4)	0.2788(3)	4.4(1)
C(213)	−0.0225(6)	0.1267(4)	0.3871(4)	5.4(1)
C(214)	0.0446(6)	0.1999(5)	0.4040(4)	5.6(1)
C(215)	0.1312(6)	0.2529(4)	0.3133(4)	5.4(1)
C(216)	0.1480(5)	0.2312(4)	0.2044(4)	4.3(1)
C(221)	0.1126(4)	0.2538(3)	−0.0375(3)	2.98(8)
C(222)	0.2443(5)	0.2798(3)	−0.1103(3)	4.03(9)
C(223)	0.2365(6)	0.3815(4)	−0.1711(4)	5.1(1)
C(224)	0.0982(6)	0.4577(3)	−0.1603(4)	4.8(1)
C(225)	−0.0333(5)	0.4333(3)	−0.0891(4)	4.6(1)
C(226)	−0.0267(4)	0.3317(3)	−0.0284(3)	3.70(9)

Table 2

Selected bond lengths (Å) and angles (deg) for trans-[Ru(C≡CC$_6$H$_4$NO$_2$-4)$_2$ (dppm)$_2$] (1) and trans-[Ru(C≡CPh)$_2$(dppe)$_2$] (5)

	1	5 [a,b]	
Ru(1)–P(1)	2.344(1)	2.363(2)	2.360(2)
Ru(1)–P(2)	2.3341(9)	2.356(2)	2.362(2)
Ru(1)–C(1)	2.051(3)	2.064(5)	2.061(5)
C(1)–C(2)	1.207(4)	1.194(7)	1.207(7)
C(2)–C(3)	1.427(5)	1.449(8)	1.434(7)
Ru–C(1)–C(2)	178.3(3)	174.3(5)	178.1(5)
C(1)–C(2)–C(3)	173.9(4)	168.3(6)	174.4(6)

[a] Non-centrosymmetric molecule: atoms relabelled as in 1. [b] Ref. [14].

values indicates that removal of electron density from the acetylide linkage becomes less marked on chain lengthening. ^{31}P NMR spectra contain singlet resonances at −3.3 (1), −2.9 (2) and −3.0 (3) ppm, consistent with trans geometry about the octahedral ruthenium.

It is believed that preparation of 1, 2, and 3 proceeds in a stepwise fashion, by way of intermediate mono(vinylidene), mono(acetylide), and (vinylidene)-(acetylide) intermediates. With this in mind, the synthesis of an unsymmetric bis(acetylide) complex was pursued, utilizing a mono(acetylide) precursor (Scheme 2).

The order of addition of acetylene is important. Attempts to synthesize the (phenylacetylide)(4-nitrophenylacetylide) complex 4 from the chloro(4-nitrophenylacetylide) complex were unsuccessful; instead, a small amount of 1 was obtained. In contrast, addition of 4-nitrophenylacetylene to the (chloro)(phenylacetylide) complex afforded 4 in 30% yield, together with a small amount of 1. The ^{31}P NMR of complex 4 contains a singlet at −3.1 ppm, confirming the phosphines are trans-disposed.

The FAB MS contains a molecular ion, with fragmentation proceeding by sequential loss of phenylacetylide and 4-nitrophenylacetylide, the order of fragmentation being consistent with the nitrophenylacetylide as the more strongly bound ligand.

2.2. X-ray structural studies of trans-[Ru(C≡CC$_6$H$_4$R-4)$_2$(dppm)$_2$] (R = NO$_2$ (1), C$_6$H$_4$NO$_2$-4 (2))

X-ray structural studies of both 1 and 2 were carried out. Problems associated with that of 2 are detailed in the Experimental details section; this structural determination was sufficient only to establish the atom–atom connectivity, with the relative precision rendering discussion of bond lengths and angles meaningless. The solid state structure of 1 is shown in Fig. 1, atomic coordinates are listed in Table 1 and selected bond lengths and angles are given in Table 2; the latter table

also contains comparable data from *trans*-[Ru(C≡CPh)₂(dppe)₂] (5) [14], the only previous report of a structural study of a bis(acetylide)bis(diphosphine)-ruthenium complex.

The structural study confirms the octahedral geometry at ruthenium and *trans*-disposed acetylide ligands, and reveals that the ruthenium atom in 1 sits on a crystallographic inversion centre; consequently, only the unique half of the molecule is considered. Important bond lengths and angles are similar to those of 5; significantly, the strong acceptor nitro group has little effect on acetylide geometry in the ground state structure. The insensitivity of Ru–C(1) distance to acetylide substituent is important when combining molecular fragments for the semiempirical calculations detailed below. For 1, distances and angles within the phosphine and acetylide ligands are not unusual.

The molecular structure of 2 is shown in Fig. 2, showing two distinct molecules. As mentioned above, the structure is useful only insofar as it confirms the atomic connectivity. As with the previously structurally characterized *trans*-[Ru(C≡CC₆H₄C₆H₄NO₂-4,4')Cl-(dppm)₂] [1], the phenylene groups in the nitrobiphenylacetylide ligands are not coplanar.

2.3. Semiempirical calculations

We have previously utilized the computationally-efficient semiempirical routine ZINDO to evaluate quadratic molecular nonlinearities of mono(acetylide) complexes of (cyclopentadienyl)bis(phosphine)ruthenium(II) [9] and chlorobis(diphosphine)ruthenium(II) [1]; such studies have validity in a relative sense for a systematically varied system. We have now extended calculations for
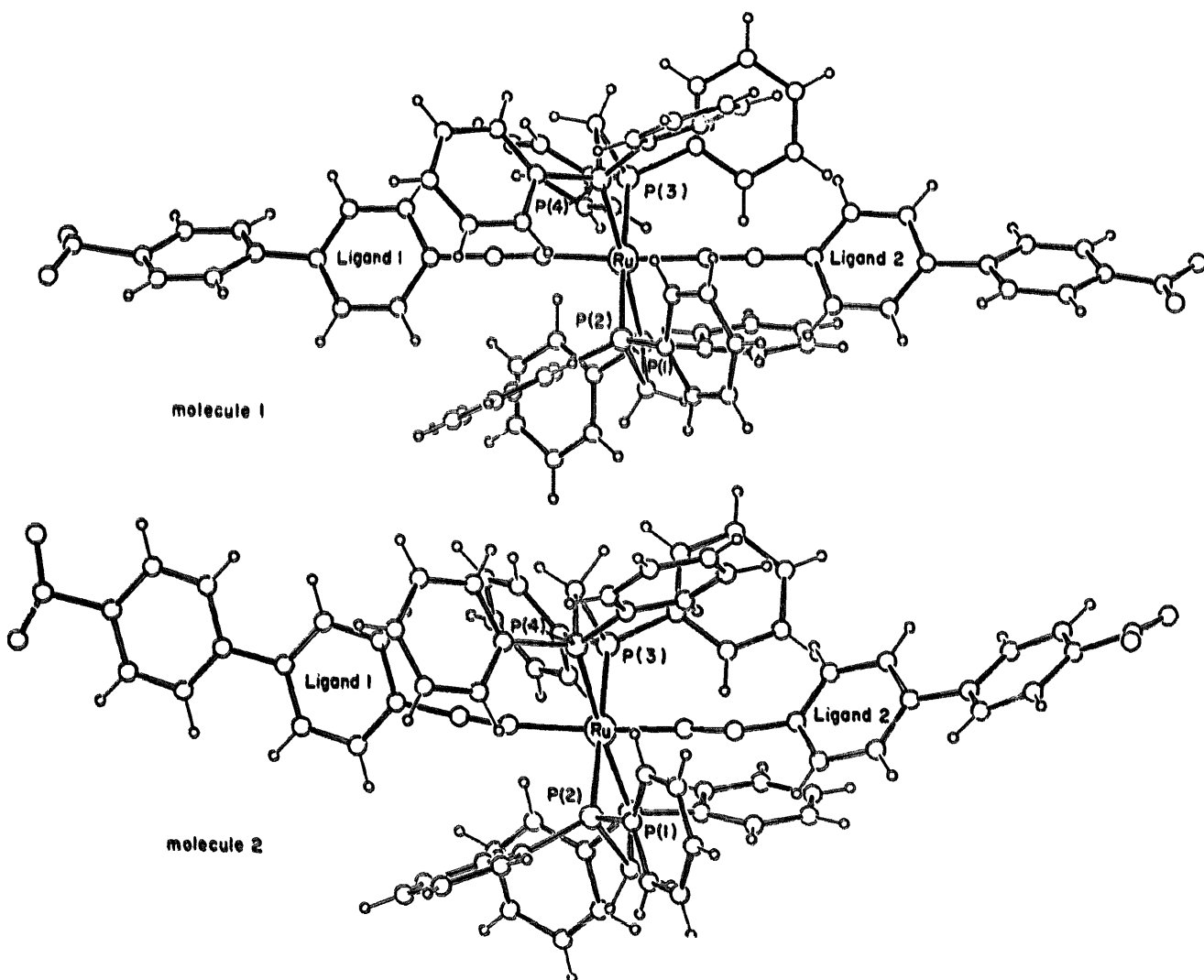

Fig. 2. Molecular geometry and atomic labelling scheme for *trans*-[Ru(C≡CC₆H₄C₆H₄NO₂-4,4')₂(dppm)₂] (2), showing the two non-equivalent molecules.

Table 3
Calculated β_{vec} (10^{-30} cm^5 esu^{-1}; $\hbar\omega$ = 0.65 eV)

Complex	β_{vec}
trans-[Ru(C≡CPh)Cl(dppm)$_2$] [a]	−13
trans-[Ru(C≡CC$_6$H$_4$NO$_2$-4)Cl(dppm)$_2$] [a]	34
trans-[Ru(C≡CC$_6$H$_4$NO$_2$-4)$_2$(dppm)$_2$] (1) [b]	0
trans-[Ru(C≡CPh)(C≡CC$_6$H$_4$NO$_2$-4)(dppm)$_2$] (4) [b]	32
[Ru(C≡CPh)(PPh$_3$)$_2$(η^5-C$_5$H$_5$)] [c]	2
[Ru(C≡CPh)(PMe$_3$)$_2$(η^5-C$_5$H$_5$)] [c]	5
[Ru(C≡CC$_6$H$_4$NO$_2$-4)(PPh$_3$)$_2$(η^5-C$_5$H$_5$)] [c]	29
[Ru(C≡CC$_6$H$_4$NO$_2$-4)(PMe$_3$)$_2$(η^5-C$_5$H$_5$)] [c]	31

[a] Ref. [1]. [b] This work. [c] Ref. [9].

the latter series of complexes to include 1 and 4; results from these calculations are summarized in Table 3.

Not surprisingly, centrosymmetric 1 has a β_{vec} of 0. Replacement of one of the 4-nitrophenylacetylide ligands in 1 by chloro to give trans-[Ru(C≡CC$_6$H$_4$NO$_2$-4)Cl(dppm)$_2$] removes the centrosymmetry and affords a donor–acceptor complex with a β_{vec} value of 34 × 10^{-30} cm^5 esu^{-1}. Replacement of one of the 4-nitrophenylacetylide ligands in 1 by phenylacetylide to give 4 also gives a donor–acceptor organometallic complex; its β_{vec} value of 32 × 10^{-30} cm^5 esu^{-1} suggests that the chloro ligand is electronically similar to the phenylacetylide ligand for these complexes. However, the complex bearing both chloro and phenylacetylide ligands in a mutually trans-arrangement, trans-[Ru(C≡CPh)Cl(dppm)$_2$], has a β_{vec} value of − 13 × 10^{-30} cm^5 esu^{-1}. This is the first demonstration of the non-additivity of ligands for quadratic hyperpolarizabilities; for ligand additivity, a β_{vec} value close to zero for trans-[Ru(C≡CPh)Cl(dppm)$_2$] would be observed. It is perhaps significant that the π-donating ligands under consideration here are disposed in a mutually trans arrangement. Although prevailing wisdom is that the effects exerted by assembled ligands on electronic properties of a coordination complex are additive [16], Heath and Humphrey have previously pointed out that strongly π-accepting trans-disposed ligands can result in attenuated ligand additivity effects when measured electrochemically [17]. In the pseudo-octahedral (cyclopentadienyl)bis(phosphine)ruthenium acetylide complexes we examined earlier [9], ligand additivity on β_{vec} was observed (see Table 3); phosphine or acetylide replacement lead to consistent variation in the computationally-obtained molecular quadratic hyperpolarizability.

For the latter system, though, the cyclopentadienyl group can be considered to occupy three facially-disposed coordination sites, with the phosphine and acetylide ligands mutually cis. At a simplistic level, then, ligand additivity for calculated β_{vec} in ruthenium acetylide systems occurs when the ligands are not competing for the same metal-based orbital. Verification of this observation could be achieved by examination of either (pentamethylcyclopentadienyl)bis(phosphine)ruthenium acetylides or cis-bis(acetylide)bis(diphosphine)ruthenium complexes. Studies toward this goal are currently underway.

3. Experimental details

3.1. General conditions

All reactions were performed under a nitrogen atmosphere with the use of Schlenk techniques unless otherwise stated. CH$_2$Cl$_2$ was dried by distilling over CaH$_2$; other solvents were used as-received. Column chromatography was performed using Merck aluminium oxide 90 active basic (activity stage II, 70–230 mesh ASTM). 'Pet. spirit' refers to a fraction of petroleum ether of boiling range 60–80°C.

3.2. Instruments

Mass spectra were recorded using a VG ZAB 2SEQ instrument (30 kV Cs$^+$ ions, current 1 mA, accelerating potential 8 kV, 3-nitrobenzyl alcohol matrix) at the Research School of Chemistry, Australian National University; peaks are reported as m/z (assignment, relative intensity). Microanalyses were carried out at the Research School of Chemistry, Australian National University. Infrared spectra were recorded as KBr pellets using a Perkin–Elmer 1600 FT-IR or a Perkin–Elmer System 2000 FT-IR. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using Varian Gemini-300 or Varian 400 FT NMR spectrometers and are referenced to residual CHCl$_3$ (7.24 ppm), CDCl$_3$ (77.0 ppm) or external 85% H$_3$PO$_4$ (0.0 ppm) respectively. Spectral assignments follow the numbering scheme shown in Fig. 3.
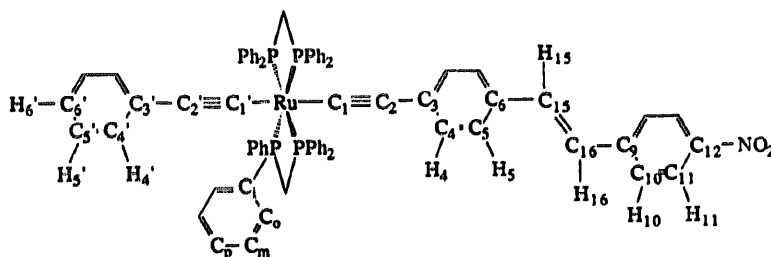

Fig. 3.

3.3. Starting materials

The following were prepared by literature methods: cis-[RuCl$_2$(dppm)$_2$] [18], 4-ethynylnitrobenzene [19], 4,4'-HC≡CC$_6$H$_4$C$_6$H$_4$NO$_2$ [20], (E),4,4'-HC≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$ [21] and trans-[Ru(C≡CPh)Cl(dppm)$_2$] [1,15]. Phenylacetylene and NaPF$_6$ (Aldrich) were used as received.

3.4. Preparation of σ-acetylide complexes

3.4.1. trans-[Ru(C≡CC$_6$H$_4$NO$_2$-4)$_2$(dppm)$_2$] (1)

A mixture of cis-[RuCl$_2$(dppm)$_2$] (340 mg, 0.36 mmol), 4-HC≡CC$_6$H$_4$NO$_2$ (110 mg, 0.75 mmol), NaPF$_6$ (125 mg, 0.75 mmol) and NEt$_3$ (0.24 ml, 1.8 mmol) was refluxed in CH$_2$Cl$_2$ (10 ml) for 16 h. The mixture was allowed to cool to room temperature and then adsorbed onto alumina by adding the alumina to the reaction mixture and removing the solvent under vacuum. It was then placed on a short column and eluted firstly with 30% CH$_2$Cl$_2$–pet. spirit to remove any excess acetylene and then with CH$_2$Cl$_2$ to remove the product. The product was precipitated by the addition of pet. spirit to the eluate and then reducing the volume on a rotary evaporator. Upon filtering, 260 mg of red microcrystals were isolated (62%). FAB MS: 1162 ([M]$^+$, 5), 870 ([Ru(dppm)$_2$]$^+$, 20). Anal. Found: C, 67.71; H, 4.42; N, 2.20. C$_{66}$H$_{52}$N$_2$O$_4$P$_4$Ru. Calc.: C, 68.21; H, 4.51; N, 2.41%. IR (KBr): ν(C≡C) 2042 cm^{-1}. ^{1}H NMR: (δ, 300 MHz, CDCl$_3$); 7.80 (d, J_{HH} = 9 Hz, 4H, H$_5$), 7.40 to 7.06 (40H, Ph), 6.13 (d, J_{HH} = 9 Hz, 4H, H$_4$), 4.84 (m, 4H, CH$_2$). ^{13}C NMR: (δ, 75 MHz, CDCl$_3$); 142.5 (C$_6$), 137.5 (C$_3$), 134.9 (C$_1$), 133.2 (C$_0$), 129.7 (C$_4$), 129.4 (C$_p$), 127.6 (C$_m$), 123.0 (C$_5$). ^{31}P NMR: (δ, 121 MHz, CDCl$_3$): −3.3 (PPh$_2$). A crystal suitable for X-ray diffraction study was grown from CHCl$_3$–MeOH.

3.4.2. trans-[Ru(C≡CC$_6$H$_4$C$_6$H$_4$NO$_2$-4,4')$_2$(dppm)$_2$] (2)

A mixture of cis-[RuCl$_2$(dppm)$_2$] (400 mg, 0.43 mmol), 4,4'-HC≡CC$_6$H$_4$C$_6$H$_4$NO$_2$ (330 mg, 1.49 mmol) and NaPF$_6$ (210 mg, 1.25 mmol) was stirred in CH$_2$Cl$_2$ (10 ml) for 4 h. After this time, NEt$_3$ (0.48 ml, 3.6 mmol) was added and stirring continued for a further 48 h. The mixture was then adsorbed onto alumina by adding the alumina to the reaction mixture and removing the solvent under vacuum. It was placed on a short column and eluted firstly with 30% CH$_2$Cl$_2$–pet. spirit to remove any excess acetylene and then with CH$_2$Cl$_2$ to remove the product. The product was precipitated by the addition of pet. spirit to the solution and then reducing the volume using a rotary evaporator. Upon filtering, 195 mg of dark red microcrystals were isolated (35%). FAB MS: 1315 ([M]$^+$, 2), 1092 ([M − C≡CC$_6$H$_4$C$_6$H$_4$NO$_2$]$^+$, 2), 870 ([Ru(dppm)$_2$]$^+$, 4).

Anal. Found: C, 70.98; H, 4.56; N, 2.00. C$_{78}$H$_{60}$N$_2$O$_4$P$_4$Ru. Calc.: C, 71.28; H, 4.60; N, 2.13%. IR (KBr): ν(C≡C) 2064 cm^{-1}. ^{1}H NMR: (δ, 300 MHz, CDCl$_3$); 8.23 (d, J_{HH} = 9 Hz, 4H, H$_{11}$), 7.67 (d, J_{HH} = 9 Hz, 4H, H$_{10}$), 7.50 to 7.08 (44H, Ph), 6.32 (d, J_{HH} = 9 Hz, 4H, H$_4$), 4.84 (m, 4H, CH$_2$). ^{13}C NMR: (δ, 100 MHz, CDCl$_3$); 147.8 (C$_{12}$), 146.1 (C$_9$), 135.6 (C$_1$), 133.4 (C$_0$), 131.9, 131.8 (C$_3$ and C$_6$), 130.7 (C$_4$), 129.0 (C$_p$), 127.5 (C$_m$), 126.6, 125.9 (C$_5$ and C$_{10}$), 124.1 (C$_{11}$), 116.3 (C$_2$), 52.1 (CH$_2$). ^{31}P NMR: (δ, 121 MHz, CDCl$_3$); −2.9 (PPh$_2$). A crystal suitable for X-ray diffraction study was grown from CHCl$_3$–MeOH.

3.4.3. trans-[Ru(C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$-4,4',(E))$_2$(dppm)$_2$] (3)

Using the same procedure as in 3.4.2., cis-[RuCl$_2$(dppm)$_2$] (300 mg, 0.32 mmol), (E),4,4'-HC≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$ (250 mg, 1.00 mmol), NaPF$_6$ (160 mg, 0.95 mmol) and NEt$_3$ (0.30 ml, 2.25 mmol) afforded 70 mg of dark purple microcrystals (16%). FAB MS: 1367 ([M]$^+$, 1), 869 ([Ru(dppm)$_2$]$^+$, 4). Anal. Found: C, 71.34; H, 4.59; N, 1.80. C$_{82}$H$_{64}$N$_2$O$_4$P$_4$Ru. Calc.: C, 72.08; H, 4.72; N, 2.05%. IR (KBr): ν(C≡C) 2058 cm^{-1}. ^{1}H NMR: (δ, 300 MHz, CDCl$_3$); 8.18 (d, J_{HH} = 9 Hz, 4H, H$_{11}$), 7.55 (d, J_{HH} = 9 Hz, 4H, H$_{10}$), 7.50 to 7.07 (46H, Ph partially obscuring H$_{16}$), 8.46 (d, J_{HH} = 15 Hz, 4H, H$_{15}$), 6.23 (d, J_{HH} = 8 Hz, 4H, H$_4$), 4.83 (m, 4H, CH$_2$). ^{13}C NMR: (δ, 100 MHz, CDCl$_3$); 133.5 (C$_0$), 129.1 (C$_p$), 127.5 (C$_m$), 124.2 (C$_{11}$). ^{31}P NMR: (δ, 121 MHz, CDCl$_3$); −3.0 (PPh$_2$).

3.4.4. trans-[Ru(C≡CPh)(C≡CC$_6$H$_4$NO$_2$-4)(dppm)$_2$] (4)

A mixture of trans-[Ru(C≡CPh)Cl(dppm)$_2$] (235 mg, 0.25 mmol), 4-HC≡CC$_6$H$_4$NO$_2$ (40 mg, 0.27 mmol), NaPF$_6$ (80 mg, 0.48 mmol) and NEt$_3$ (0.350 ml, 2.6 mmol) was stirred in CH$_2$Cl$_2$ (20 ml) for 7 h. The resultant mixture was adsorbed onto alumina by adding the alumina to the reaction mixture and removing the solvent under vacuum. It was then placed on a short column and eluted firstly with 25% CH$_2$Cl$_2$–pet. spirit to remove any excess acetylene and then with 35% CH$_2$Cl$_2$–pet. spirit to remove the product. The product was precipitated by the addition of pet. spirit to the eluate and then reducing the volume on a rotary evaporator. Upon filtering, 80 mg of dark red powder was isolated (30%). FAB MS: 1118 ([M]$^+$, 2), 1016 ([M − C≡CPh]$^+$, 2), 870 ([Ru(dppm)$_2$]$^+$, 3). Anal. Found: C, 70.98; H, 4.66; N, 1.02. C$_{66}$H$_{53}$NO$_2$P$_4$Ru. Calc.: C, 70.96; H, 4.78; N, 1.25%. IR (KBr): ν(C≡C) 2055 cm^{-1}. ^{1}H NMR: (δ, 300 MHz, CDCl$_3$); 7.78 (d, J_{HH} = 9 Hz, 2H, H$_5$), 7.49 to 7.06 (40H, Ph), 6.92 (m, 3H, H$_5'$ and H$_6'$), 6.30 (d, J_{HH} = 7 Hz, 2H, H$_4'$), 6.08 (d, J_{HH} = 9 Hz, 2H, H$_4$), 4.83 (m, 4H, CH$_2$). ^{13}C NMR: (δ, 100 MHz, CDCl$_3$); 142.1 (C$_6$), 137.9 (C$_3$), 135.4

(C_i), 133.3 (C_o), 130.6 (C_5), 130.0 $(C_{4'})$, 129.7 (C_4), 127.5 (C_m), 127.0 $(C_{5'})$, 123.0 (C_5), 122.7 (C_6), 52.1 (CH_2). ^{31}P NMR: $(\delta, 121$ MHz, $CDCl_3)$; -3.1 (PPh_2). Further elution of the column with CH_2Cl_2 afforded 20 mg of the complex *trans*-[Ru(C≡CC$_6$H$_4$NO$_2$-4)$_2$(dppm)$_2$] (1) (7%), characterized by comparison of its ^1H and ^{31}P NMR spectra with those of an authentic sample.

3.5. X-ray structure determinations

3.5.1. General conditions

Unique diffractometer data sets $(T \approx 295$ K; monochromatic Mo Kα radiation $(\lambda = 0.7107_3$ Å); $2\theta-\theta$ scan mode, $2\theta_{max} = 50°)$ were obtained, yielding 4883 (1) and 8002 (2) independent reflections, 3806 (1) and 2541 (2) of these with $I \geq 3\sigma(I)$ being considered 'observed' and used in full matrix (1)/large block (2) least squares refinement; a Gaussian absorption correction was applied to 2 ($A^*_{min,max} = 1.05$, 1.16) and an empirical ψ-type absorption correction was applied to 1 $(T_{min,max} = 0.84$, 1.00). In the case of 1, anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. For 2, only ruthenium was refined isotropically. Conventional residuals R, R_w on $|F|$ at convergence were 0.096, 0.093 (2) (both hands), and 0.035, 0.037 (1); statistical weights derivative of $\sigma^2(I)$ $= \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were used for 2, whereas in 1 the weighting function $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(C + 4B) + (pF_o^2)^2]/Lp^2$ (σ is the scan rate, C is the peak count, B is the background count, and $p = 0.001$ determined experimentally from standard reflections) was employed. Computation used the XTAL 3.2 program system implemented by Hall et al. [22] (2), and the teXsan package [23] (1). Pertinent results are given in the figures and tables. Tables of non-hydrogen atom coordinates and thermal parameters (2) hydrogen atom coordinates and thermal parameters and complete lists of bond lengths and angles for non-hydrogen atoms (1 and 2) have been deposited at the Cambridge Crystallographic Data Centre.

3.5.2. Unusual features / variations in procedure

A combination of small crystal, large cell, non-centrosymmetric space group, long axis, and pseudo-symmetry resulted in a very imprecise structural determination of 2. All phenyl groups were refined as rigid bodies. Acetylide C≡C carbon atom thermal parameters refined unsatisfactorily and were consequently fixed. The structural study of 2 is inferior and useful only insofar as it establishes non-hydrogen connectivity and the lack of coplanarity in the biphenylene groups.

3.5.3. Crystal data

For 1: $C_{66}H_{52}N_2O_4P_4Ru$, $M = 1162.1$. Triclinic, space group $P\bar{1}$ (No. 2), $a = 9.729(5)$, $b = 12.564(5)$, $c = 12.674(4)$ Å, $\alpha = 81.22(3)$, $\beta = 69.24(3)$, $\gamma = 72.16(3)°$, $V = 1377(1)$ Å^3. $D_c = 1.401$ g cm^{-3} $(Z = 1)$; $F(000) = 598$; $\mu_{Mo} = 4.42$ cm^{-1}; specimen: $0.30 \times 0.10 \times 0.10$ mm^3; $T_{min,max} = 0.84$, 1.00.

For 2: $C_{78}H_{60}N_2O_4P_4Ru$, $M = 1314.4$. Orthorhombic, space group $Pca2_1$ (No. 29), $a = 19.455(7)$, $b = 16.575(7)$, $c = 40.28(5)$ Å, $V = 12987(17)$ Å^3. $D_c = 1.344$ g cm^{-3} $(Z = 8)$; $F(000) = 5424$; $\mu_{Mo} = 3.9$ cm^{-1}; specimen: $0.15 \times 0.24 \times 0.15$ mm^3.

3.6. Computational details

Results were obtained using ZINDO (June 1994 version) from Biosym Technologies, San Diego, CA, USA [24], implemented on a Silicon Graphics INDY workstation without parameter manipulation or basis function alteration. The input for the calculation of 1 was the atomic coordinates obtained from the X-ray diffraction structural determination; for 4, coordinates were produced from a combination of fragments of related structurally characterized complexes (Ru(C≡CC$_6$H$_4$NO$_2$-4)(dppm)$_2$ from *trans*-[Ru(C≡CC$_6$H$_4$NO$_2$-4)$_2$(dppm)$_2$] (1), and C≡CPh from *trans*-[Ru(C≡CPh)$_2$(dppe)$_2$] (5) [14]) using the 'builder' routine in the molecular modeling package Insight II, with Ru–C distances of 2.05 Å being assumed. CI calculations included single excitations; basis set sizes were increased progressively for all calculations until convergence $(\pm 2 \times 10^{-30}$ cm^5 esu$^{-1})$ in the computed β_{vec} value was reached (150–250 excited configurations).

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