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Rigid rod σ-acetylide complexes of iron, ruthenium and osmium *

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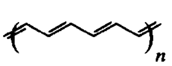
Abstract

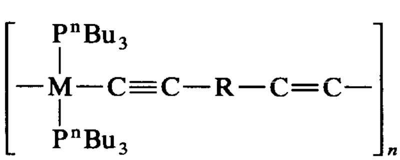
The synthetic utility of bis(trimethylstannyl)alkynyls in the preparation of Group 8 metal (Fe^{2+}, Ru^{2+}, Os^{2+}) σ-acetylide monomeric, $M(DEPE)_2(-C\equiv C-C_6H_5)_2$ ($M = Fe^{2+}$, Ru^{2+}; DEPE = 1,2-bis(diethylphosphino)ethane), $Ru(DPPE)_2(-C\equiv C-C_6H_5)_2$ (DPPE = 1,2-bis(diphenylphosphino)ethane), $Os(DPPM)_2(-C\equiv C-C_6H_5)_2$ (DPPM = 1,2-bis(diphenylphosphino)methane) and polymeric, $[-M(DEPE)_2-C\equiv C-R-C\equiv C-]_n$ ($M = Fe^{2+}$, Ru^{2+}), $[-Os(DPPM)_2-C\equiv C-R-C\equiv C-]_n$ ($R = p\text{-}C_6H_4\text{-}C_6H_4\text{-}p$, $p\text{-}C_6H_4$, $p\text{-}C_6H_2(CH_3)_2$) complexes is demonstrated. The linear arrangement of the acetylenic units around octahedral metal centres is confirmed by a single crystal X-ray structure determination of the model complex *trans*-$[Ru(DPPE)_2(-C\equiv C-C_6H_5)_2]$.

1. Introduction

Organic polymers with highly delocalized π-electrons (*e.g.* polyacetylene (**1**)) are good candidates in respect of properties such as third order nonlinear optical effects (χ^3) for possible applications in the materials industry [1]. Incorporation of transition metals into the conjugation backbone, as for example in transition metal σ-acetylide complexes (**2**), is expected to enhance these properties as well as increase their solubility in common organic solvents to facilitate processing to desired materials.



(1)



$$\left[-\underset{P^nBu_3}{\overset{P^nBu_3}{M}}-C\equiv C-R-C=C-\right]_n$$

$(R = p\text{-}C_6H_4;\ p\text{-}C_6H_4\text{-}C_6H_4\text{-}p)$

(2)

Such complexes were first synthesized for Group 10 metals (Ni^{2+}, Pd^{2+} and Pt^{2+}) by Hagihara et al. [2], and were subsequently found [3] to exhibit third-order hyperpolarizabilities much higher than those of their purely organic counterparts. The extent of conjugation in these rigid rod organometallic complexes may be tailored by introducing a wide variety of alkynes and transition metals in varying oxidation states. The original synthetic route of dehydrohalogenation (eqn. (1)) reported by Hagihara and co-workers [2] has its limitations since the metal halide complexes other than those of Pt^{2+} and Pd^{2+} are unstable in the amine solvents. We have recently developed [4] a new synthetic procedure which employs bis-trimethylstannyl-alkynes ($Me_3Sn-C\equiv C-R-C\equiv SnMe_3$) as precursors (eqn. (2)) for a variety of transition metal σ-acetylide complexes. In this contribution, we present an overview of our recent results on Group 8 transition metal-containing mono-, oligo- and polyyne organometallic complexes.

$$MCl_2(P^nBu_3)_2 + H-C\equiv C-R-C\equiv C-H \xrightarrow[CuI]{NR_3} [-(P^nBu_3)_2M-C\equiv C-R-C\equiv C-]_n \quad (1)$$

$$MCl_2(PR_3)_m + Me_3Sn-C\equiv C-R-C\equiv C-SnMe_3 \longrightarrow [-(PR_3)_mM-C\equiv C-R-C\equiv C-]_n + 2\,SnMe_3Cl \quad (2)$$

2. Results and discussion

Formation of a transition metal-to-acetylene σ-bond by a metathesis reaction of trimethylstannyl-alkyne with

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* Dedicated to Professor Michael F. Lappert, F.R.S. on the occasion of his 65th birthday.

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TABLE 1. Atomic coordinates and equivalent isotropic displacement coefficients (Å^2) for *trans*-[Ru(C≡CPh)$_2$(dppe)$_2$]

	x	y	z	U_{eq}
Ru	0.49315(4)	0.13833(3)	0.25858(2)	0.0295(3)
P(1)	0.47201(14)	0.26847(11)	0.16494(6)	0.0343(9)
P(2)	0.35330(14)	0.04123(11)	0.22485(6)	0.0352(9)
P(3)	0.50668(13)	0.00621(11)	0.35243(7)	0.0362(9)
P(4)	0.62201(13)	0.24010(11)	0.29637(6)	0.0346(8)
C(13)	0.3411(5)	0.2263(4)	0.1343(2)	0.043(4)
C(23)	0.2532(5)	0.1484(4)	0.1851(3)	0.043(4)
C(33)	0.6071(6)	0.0611(4)	0.3944(3)	0.049(4)
C(43)	0.7052(5)	0.1371(4)	0.3480(3)	0.044(3)
C(01)	0.3286(5)	0.2062(4)	0.3035(2)	0.034(3)
C(02)	0.2343(5)	0.2477(4)	0.3305(3)	0.039(3)
C(03)	0.1302(5)	0.3049(4)	0.3631(3)	0.041(3)
C(04)	0.1347(6)	0.3300(5)	0.4209(3)	0.055(4)
C(05)	0.0379(7)	0.3900(5)	0.4501(3)	0.067(5)
C(06)	−0.0646(7)	0.4264(6)	0.4239(4)	0.077(5)
C(07)	−0.0727(7)	0.3996(6)	0.3689(4)	0.080(5)
C(08)	0.0221(6)	0.3405(5)	0.3388(3)	0.062(4)
C(1)	0.6630(5)	0.0673(4)	0.2211(2)	0.037(3)
C(2)	0.7596(5)	0.0191(5)	0.2042(3)	0.044(4)
C(3)	0.8598(5)	−0.0539(5)	0.1808(3)	0.054(3)
C(4)	0.9027(7)	−0.0483(7)	0.1169(4)	0.090(6)
C(5)	0.9909(9)	−0.1277(9)	0.0973(5)	0.113(7)
C(6)	1.0345(8)	−0.2103(8)	0.1409(6)	0.107(6)
C(7)	0.9950(7)	−0.2144(7)	0.2020(5)	0.091(5)
C(8)	0.9092(6)	−0.1380(5)	0.2233(4)	0.066(4)
C(111)	0.4228(6)	0.4096(4)	0.1712(2)	0.040(4)
C(112)	0.2956(6)	0.4334(5)	0.1963(3)	0.052(4)
C(113)	0.2578(8)	0.5371(5)	0.2053(3)	0.070(6)
C(114)	0.3445(10)	0.6172(6)	0.1888(3)	0.083(8)
C(115)	0.4701(9)	0.5971(5)	0.1640(3)	0.075(7)
C(116)	0.5102(7)	0.4917(4)	0.1548(3)	0.054(5)
C(121)	0.5970(6)	0.2984(4)	0.0925(2)	0.042(4)
C(122)	0.5694(7)	0.3584(5)	0.0359(3)	0.062(5)
C(123)	0.6636(9)	0.3867(6)	−0.0172(3)	0.079(7)
C(124)	0.7857(9)	0.3573(6)	−0.0160(3)	0.081(7)
C(125)	0.8149(7)	0.2955(6)	0.0393(4)	0.085(5)
C(126)	0.7209(6)	0.2660(5)	0.0928(3)	0.063(5)
C(211)	0.2346(5)	−0.0512(4)	0.2813(2)	0.039(3)
C(212)	0.2498(6)	−0.1643(5)	0.2915(3)	0.054(4)
C(213)	0.1590(7)	−0.2333(6)	0.3324(3)	0.070(5)
C(214)	0.0512(7)	−0.1905(7)	0.3648(3)	0.074(5)
C(215)	0.0345(7)	−0.0785(7)	0.3564(3)	0.071(4)
C(216)	0.1260(6)	−0.0091(5)	0.3148(3)	0.056(4)
C(221)	0.4064(6)	−0.0319(4)	0.1606(3)	0.043(4)
C(222)	0.5333(6)	−0.0393(5)	0.1316(3)	0.057(5)
C(223)	0.5704(8)	−0.0873(6)	0.0803(3)	0.079(6)
C(224)	0.4828(8)	−0.1249(5)	0.0556(3)	0.072(7)
C(225)	0.3574(8)	−0.1177(5)	0.0830(3)	0.068(6)
C(226)	0.3178(6)	−0.0716(4)	0.1346(3)	0.054(5)
C(311)	0.3645(5)	−0.0319(5)	0.4161(2)	0.044(3)
C(312)	0.3192(6)	−0.1363(5)	0.4356(3)	0.056(4)
C(313)	0.2103(7)	−0.1605(7)	0.4833(3)	0.078(5)
C(314)	0.1467(7)	−0.0786(9)	0.5112(3)	0.084(4)
C(315)	0.1905(7)	0.0255(8)	0.4907(3)	0.079(5)
C(316)	0.2984(6)	0.0499(6)	0.4440(3)	0.059(4)
C(321)	0.5809(5)	−0.1291(4)	0.3470(3)	0.040(3)
C(322)	0.5778(5)	−0.1731(4)	0.2963(3)	0.050(4)
C(323)	0.6259(6)	−0.2774(5)	0.2923(4)	0.073(5)
C(324)	0.6790(7)	−0.3386(5)	0.3417(4)	0.083(6)
C(325)	0.6839(7)	−0.2969(6)	0.3916(4)	0.079(6)
C(326)	0.6349(6)	−0.1934(5)	0.3956(3)	0.060(5)
C(411)	0.7544(5)	0.3246(5)	0.2442(2)	0.042(4)
C(412)	0.7499(6)	0.4382(5)	0.2332(3)	0.059(4)
C(413)	0.8498(7)	0.4992(6)	0.1932(4)	0.079(5)
C(414)	0.9539(7)	0.4477(7)	0.1633(4)	0.083(5)
C(415)	0.9599(7)	0.3351(7)	0.1743(4)	0.075(4)
C(416)	0.8617(6)	0.2738(5)	0.2139(3)	0.055(4)
C(421)	0.5447(5)	0.3314(4)	0.3484(3)	0.040(3)
C(422)	0.5707(6)	0.3272(5)	0.4074(3)	0.054(4)
C(423)	0.5099(7)	0.3988(6)	0.4434(3)	0.068(6)
C(424)	0.4248(7)	0.4756(6)	0.4218(3)	0.071(5)
C(425)	0.3978(6)	0.4815(5)	0.3637(3)	0.061(5)
C(426)	0.4566(5)	0.4096(4)	0.3271(3)	0.048(4)

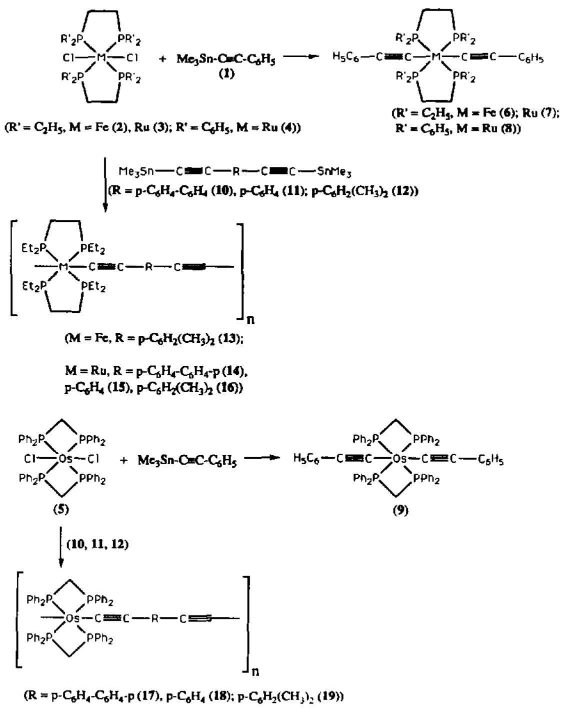
a metal halide (eqn. (3)) was first demonstrated by Lappert and co-workers in 1973 [5].

$$L_nM{-}Cl + Me_3Sn{-}C{\equiv}C{-}C_6H_5 \longrightarrow L_nM{-}C{\equiv}C{-}C_6H_5 + SnMe_3Cl \quad (3)$$

(M = Rh, Ir)

We were intrigued by the possibility of forming transition metal σ-alkyne oligomeric and polymeric complexes *via* the above reaction pathway starting from the appropriate bis-trimethylstannyl-alkynes and metal dihalides (eqn. (2)). This route proved to provide a very useful synthetic procedure for a variety of Group 9 and 10 metal σ-acetylide monomeric, oligomeric, and polymeric complexes in excellent yields [4]. Since we were interested in examining the role of the metal (with square planar and octahedral environments) in determining the backbone conjugation in such complexes, we have now extended our procedure to include metals of Group 8 (Fe^{2+}, Ru^{2+}, Os^{2+}) in the linear organometallic chains.

Reaction of a slight excess of $Me_3Sn{-}C{\equiv}C{-}C_6H_5$ (**1**) with the metal dihalide complexes ($MCl_2(DEPE)_2$), M = Fe^{2+} (**2**), Ru^{2+} (**3**), $RuCl_2(DPPE)_2$ (**4**), $OsCl_2(DPPM)_2$ (**5**) in the presence of a catalytic amount of CuI (Scheme 1) gave the monomeric metal-bis-acetylide complexes, $[M(DEPE)_2({-}C{\equiv}C{-}C_6H_5)_2]$ (M = Fe^{2+} (**6**); Ru^{2+} (**7**)), $[Ru(DPPE)_2({-}C{\equiv}C{-}C_6H_5)_2]$ (**8**), $[Os(DPPM)_2({-}C{\equiv}C{-}C_6H_5)_2]$ (**9**) in good yields. The complex $[Fe(DEPE)_2({-}C{\equiv}C{-}C_6H_5)_2]$ was reported earlier, and was prepared from $Fe(DEPE)_2(H)_2$ and phenylacetylene [6]. A similar bis(acetylide) complex of Ru-containing mixed auxiliary ligands on Ru^{2+}, $[Ru(CO)_2(PEt_3)_2({-}C{\equiv}C{-}C_6H_5)_2]$, was prepared recently by Carty *et al.* [7]. The polymeric complexes, $[{-}M(DEPE)_2{-}C{\equiv}C{-}R{-}C{\equiv}C{-}]_n$ (R = p-$C_6H_2(CH_3)_2$, M = Fe^{2+} (**13**); R = p-C_6H_4-C_6H_4-p, p-C_6H_4, p-$C_6H_2(CH_3)_2$), M = Ru^{2+} (**14–6**); $[{-}Os(DPPM)_2{-}C{\equiv}C{-}R{-}C{\equiv}C{-}]_n$ (R = p-C_6H_4-C_6H_4-p, p-C_6H_4, p-$C_6H_2(CH_3)_2$) (**17–19**) were prepared by the reaction



Scheme 1.

of an equimolar quantity of the metal dihalide complex with the appropriate bis-trimethylstannyl-alkynyl reagent (**10–12**) in the presence of a catalytic amount of CuI. The role of CuI in such reactions is not yet very well understood and is under investigation in our laboratory. These transition metal σ-acetylide complexes (except **17**) are soluble in common organic solvents, and were characterized from their analytical data, mass, ^{31}P nuclear magnetic resonance and infrared spectra. All-*trans* configuration of these compounds was clearly shown by the simple singlet pattern of their ν(C≡C) IR and ^{31}P NMR spectra. The molecular weights of the polymers were determined by the gel permeation chromatography (GPC) method [8] and indicate a high degree of polymerization.

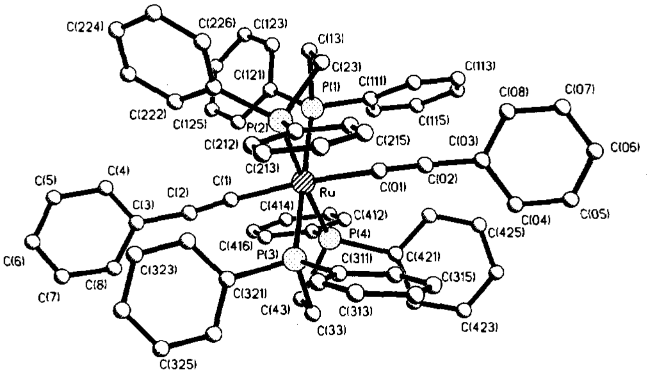


Fig. 1. Molecular structure of Ru(DPPE)$_2$(–C≡C–C$_6$H$_5$)$_2$ (**8**). Hydrogen atoms are omitted for clarity.

The molecular structure of *trans*-[Ru(DPPE)$_2$(C≡C–C$_6$H$_5$)$_2$] (**8**) is shown in Fig. 1. The atomic coordinates and selected bond parameters are listed in Tables 1 and 2, respectively. The crystal structure consists of

TABLE 2. Selected bond lengths (Å) and angles (°) for *trans*-[Ru(C≡CPh)$_2$(dppe)$_2$]

Ru–C(01)	2.061(5)	Ru–C(1)	2.064(5)
Ru–P(2)	2.356(2)	Ru–P(3)	2.360(2)
Ru–P(4)	2.362(2)	Ru–P(1)	2.363(2)
P(1)–C(121)	1.833(6)	P(1)–C(111)	1.836(5)
P(1)–C(13)	1.861(5)	P(2)–C(211)	1.833(6)
P(2)–C(221)	1.838(5)	P(2)–C(23)	1.843(5)
P(3)–C(321)	1.839(5)	P(3)–C(311)	1.841(6)
P(3)–C(33)	1.842(6)	P(4)–C(43)	1.837(5)
P(4)–C(421)	1.842(5)	P(4)–C(411)	1.844(6)
C(13)–C(23)	1.503(7)	C(33)–C(43)	1.510(7)
C(01)–C(02)	1.207(7)	C(02)–C(03)	1.434(7)
C(03)–C(08)	1.394(8)	C(03)–C(04)	1.407(8)
C(04)–C(05)	1.371(8)	C(05)–C(06)	1.363(9)
C(06)–C(07)	1.366(10)	C(07)–C(08)	1.362(8)
C(1)–C(2)	1.194(7)	C(2)–C(3)	1.449(8)
C(3)–C(4)	1.376(9)	C(3)–C(8)	1.399(9)
C(4)–C(5)	1.401(11)	C(5)–C(6)	1.374(12)
C(6)–C(7)	1.317(12)	C(7)–C(8)	1.371(9)
C(01)–Ru–C(1)	174.9(2)	C(01)–Ru–P(2)	84.30(14)
C(1)–Ru–P(2)	98.9(2)	C(01)–Ru–P(3)	91.52(14)
C(1)–Ru–P(3)	84.23(14)	P(2)–Ru–P(3)	96.63(6)
C(01)–Ru–P(4)	92.10(14)	C(1)–Ru–P(4)	84.7(2)
P(2)–Ru–P(4)	176.38(6)	P(3)–Ru–P(4)	83.08(5)
C(01)–Ru–P(1)	87.28(14)	C(1)–Ru–P(1)	97.05(14)
P(2)–Ru–P(1)	81.55(5)	P(3)–Ru–P(1)	177.91(6)
P(4)–Ru–P(1)	98.67(6)	C(121)–P(1)–C(111)	99.2(2)
C(121)–P(1)–C(13)	101.0(2)	C(111)–P(1)–C(13)	102.1(2)
C(121)–P(1)–Ru	124.5(2)	C(111)–P(1)–Ru	118.0(2)
C(13)–P(1)–Ru	108.8(2)	C(211)–P(2)–C(221)	102.5(2)
C(211)–P(2)–C(23)	102.3(2)	C(221)–P(2)–C(23)	98.2(2)
C(211)–P(2)–Ru	122.0(2)	C(221)–P(2)–Ru	122.8(2)
C(23)–P(2)–Ru	104.8(2)	C(321)–P(3)–C(311)	101.6(2)
C(321)–P(3)–C(33)	103.1(3)	C(311)–P(3)–C(33)	100.9(3)
C(321)–P(3)–Ru	119.4(2)	C(311)–P(3)–Ru	120.9(2)
C(33)–P(3)–Ru	108.1(2)	C(43)–P(4)–C(421)	103.0(3)
C(43)–P(4)–C(411)	101.9(2)	C(421)–P(4)–C(411)	101.8(2)
C(43)–P(4)–Ru	105.2(2)	C(421)–P(4)–Ru	118.8(2)
C(411)–P(4)–Ru	123.1(2)	C(23)–C(13)–P(1)	111.6(4)
C(13)–C(23)–P(2)	107.3(4)	C(43)–C(33)–P(3)	110.8(4)
C(33)–C(43)–P(4)	108.0(4)	C(02)–C(01)–Ru	178.1(5)
C(01)–C(02)–C(03)	174.4(6)	C(08)–C(03)–C(04)	116.9(5)
C(08)–C(03)–C(02)	122.3(5)	C(04)–C(03)–C(02)	120.8(5)
C(05)–C(04)–C(03)	120.4(6)	C(06)–C(05)–C(04)	121.1(6)
C(05)–C(06)–C(07)	119.3(6)	C(08)–C(07)–C(06)	120.9(7)
C(07)–C(08)–C(03)	121.3(6)	C(2)–C(1)–Ru	174.3(5)
C(1)–C(2)–C(3)	168.3(6)	C(4)–C(3)–C(8)	117.9(6)
C(4)–C(3)–C(2)	121.7(6)	C(8)–C(3)–C(2)	120.2(6)
C(3)–C(4)–C(5)	119.1(8)	C(6)–C(5)–C(4)	120.8(9)
C(7)–C(6)–C(5)	120.0(8)	C(6)–C(7)–C(8)	121.2(9)
C(7)–C(8)–C(3)	121.0(8)		

discrete monomer molecules with the ruthenium atom coordinated in a *trans* disposition to two phenylacetylides and two chelating bis-(diphenylphosphino) ethane ligands. The metal to phosphorus bond length lie within the range 2.356(2)–2.362(2) Å and metal to acetylide bond distances are 2.061(5) and 2.064(5) Å. These values are in agreement with the other structurally characterized ruthenium(II) phosphine acetylide complex [7]. The coordination geometry of the metal centre does not exhibit any large deviation from that expected for a regular octahedral coordination, with angles between *cis* donor atoms ranging from 81.55(5) to 98.9(2)° and those between *trans* atoms from 174.9(2) to 177.91(6)°. The acetylide C≡C bonds have lengths of 1.207(7) and 1.194(7) Å, and whilst these are in accord with those observed for a range of iron(II) and ruthenium(II) bis-acetylide complexes reported [6,7], there is a marginally larger distortion from linearity within the C–C≡C, M–C≡C–C chain of *trans*-[Ru(DPPE)$_2$(C≡C–C$_6$H$_5$)$_2$] than was observed previously [7]. This apparent deviation from linearity may possibly be attributable to steric pressure on the phenylacetylide ligands by the phenyl rings of the chelating phosphines.

In summary, we have prepared a series of rigid rod σ-acetylide complexes of Fe^{2+}, Ru^{2+} and Os^{2+} and have structurally characterized the first example of a linear Ru^{II}-bis-chelating phosphine-bis-acetylide complex. The analysis of their physical properties to assess the degree of conjugation in the backbone of these complexes and its comparison with those for the corresponding complexes of Group 9 and 10 metals are currently being pursued.

3. Experimental details

All reactions were carried out under nitrogen by glove box or high vacuum line techniques. Solvents were predried and distilled from appropriate drying agents. NMR spectra were recorded on a Bruker AM-400 spectrometer. $^{31}P\{^1H\}$ spectra were referenced to external trimethylphosphite and the ^1H spectra to solvent resonances. The IR spectra were recorded on a Perkin-Elmer 1710 Fourier Transform spectrometer. The molecular weights were determined by gel permeation chromatography (GPC) method. Me$_3$Sn–C≡C–C$_6$H$_5$ was prepared from phenylacetylene. Alkyne ligands (**10–12**) were prepared by published procedures [9] with some minor modifications. M(DEPE)$_2$Cl$_2$ (M = Fe^{2+}, Ru^{2+}), Ru(DPPE)$_2$Cl$_2$, Os(DPPM)$_2$Cl$_2$ were prepared by published methods [10].

3.1. X-Ray data collection, structure solution and refinement summary for trans-[Ru(DPPE)$_2$(C≡C–C$_6$H$_5$)$_2$]

The crystals for X-ray diffraction were grown by two-layer crystallization from a dichloromethane/hexane (1:1) mixture.

3.1.1. Crystal data

$C_{68}H_{58}P_4Ru$, $M = 1100.09$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.793(2)$, $b = 12.532(3)$, $c = 22.231(5)$ Å, $\alpha = 76.20(2)$, $\beta = 76.89(2)$, $\gamma = 85.62(2)°$, $V = 2843(1)$ Å^3, $Z = 2$, $D_c = 1.285$ g cm^{-3}, $F(000) = 1140$, μ(Mo-Kα) = 0.43 mm^{-1}.

A yellow rod shaped crystal of approximate dimensions 0.12 × 0.18 × 0.32 mm^3 was mounted on a glass fibre and accurate lattice parameters were determined from 30 reflections ($2\theta = 26.17$–$29.96°$). Intensity data were measured on a Siemens R3mV diffractometer using monochromated Mo-Kα radiation and ω scan mode to a maximum value for 2θ of 45°. Three standard reflections were monitored after every 97 reflections collected, and showed no significant decrease in intensity during the data collection time.

A total of 7948 reflections were measured within the range $0 \le h \le 11$, $-13 \le k \le 13$, $-23 \le l \le 23$ and averaged to yield 7470 unique reflections ($R_{int} = 0.046$) of which 5563 were judged as significant on the criterion $F_{obs} > 4\sigma(F_{obs})$. Corrections for Lorentz and polarization effects were applied, and for absorption (min, max transmission 0.892, 0.914). Structure solution was by a combination of direct methods and Fourier techniques. Anisotropic thermal motion was assumed for all non-hydrogen atoms. Full-matrix least-squares refinement on F_o^2 for all data and 669 parameters converged to $wR2 = 0.111$ (all data), conventional $R = 0.042$ (observed data), $(\Delta/\sigma)_{max} = 0.001$, GOF = 1.22. The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$, $w = 1/[\sigma^2(F_{obs}^2) + (0.0301P)^2 + 3.931P]$ where $P = (F_o^2 + F_c^2)/3$ and σ was obtained from counting statistics. A final difference electron density Fourier synthesis revealed maximum and minimum residual electron density peaks of 0.40 and -0.66 e Å^{-3}.

Additional crystallographic data including hydrogen-atom coordinates, thermal parameters and full list of the bond parameters have been deposited with the Cambridge Crystallographic Data Centre. Lists of structure factors are available from the authors.

3.2. Syntheses

Ru(DEPE)$_2$(–C≡C–C$_6$H$_5$)$_2$ (7). A mixture of *trans*-Ru(DEPE)$_2$Cl$_2$ (0.058 g, 0.10 mmol), Me$_3$Sn–C≡C–C$_6$H$_5$ (0.120 g, 0.25 mmol) and CuI (5 mg) in toluene (50 ml) was stirred under nitrogen at 80°C for 40 h. Toluene was then removed *in vacuo* and the product was isolated, after purification by column chromatography on neutral grade I alumina using dichloromethane as eluant. Recrystallization from a dichloromethane/hexane (1:1) mixture gave a dark yellow solid in 60% yield.

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): 95.4 ppm (s). ν(C≡C) (CH_2Cl_2): 2054 cm^{-1}. Mass spectrum (+FAB, *m/z*) of parent ion: found 716; calcd. 715.8. Anal. Found C, 60.47; H, 8.14. $C_{36}H_{58}P_4Ru$ calcd.: C, 60.40; H, 8.14%.

The other bis-acetylide complexes were prepared by following the same general procedure except that in the case of **8**, the reaction was carried out in dichloromethane instead of toluene.

Fe(DEPE)$_2$(–C≡C–C_6H_5)$_2$ (**6**). Orange solid, 80% yield. ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz). 68.8 ppm (s). ^{1}H NMR (C_6D_6, 400 MHz): 1.14 (s, CH_3); 1.74, 2.44 (s, CH_2); 7.17, 7.59 (m, CH). ν(C≡C) (Nujol): 2038 cm^{-1}. Mass spectrum (+FAB) of parent ion: found 671; calcd. 670.6. Anal. Found C, 65.10; H, 8.79. $C_{36}H_{58}P_4Fe$ calcd.: C, 64.49; H, 8.66%.

Ru(DPPE)$_2$(–C≡C–C_6H_5)$_2$ (**8**). Yellow solid, 45% yield. ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): 88.0 ppm (s). ν(C≡C) (CH_2Cl_2) 2061 cm^{-1}. Mass spectrum (+FAB) of parent ion: found 1100.1; calcd. 1100.1. Anal. Found C, 74.67; H, 5.19. $C_{68}H_{58}P_4Ru$ calcd.: C, 74.24; H, 5.31%.

Os(DPPM)$_2$(–C≡C–C_6H_5)$_2$ (**9**). Yellow solid, 50% yield. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): 195.0 ppm (s). ν(C≡C) (CH_2Cl_2) 2069 cm^{-1}. Mass spectrum (+FAB) of parent ion: found 1161.2; calcd. 1161.2. Anal. Found C, 68.91; H, 4.75. $C_{66}H_{54}P_4Os$ calcd.: C, 68.26; H, 4.69%.

[–Os(DPPM)$_2$–C≡C-*p*-C_6H_4–C≡C–]$_n$ (**18**). A solution of Os(DPPM)$_2$Cl$_2$ (0.2116 g, 0.2 mmole), Me_3Sn–C≡C–C_6H_4–C≡C–$SnMe_3$ (0.090 g, 0.2 mmol) and CuI (5–6 mg) in toluene (60 ml) was stirred at 105°C for 48 h. The mixture was then cooled to room temperature and passed through an alumina column with dichloromethane as eluant. The volume of dichloromethane eluant was reduced to 5 ml *in vacuo* to give the polymer in 70% yield. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): 193.0 ppm (s). ν(C≡C) (CH_2Cl_2) 2064 cm^{-1}. Anal. Found C, 66.94; H, 4.51. $C_{60}H_{48}OsP_4$ calcd.: C, 66.53; H, 4.47%. $M_w = 24754$ ($n_w = 23$).

The other polymeric complexes were prepared by the same general procedure.

[–Fe(DEPE)$_2$–C≡C-*p*-$C_6H_2(CH_3)_2$–C≡C–]$_n$ (**13**). Orange yellow solid, 60% yield. ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): 69.0 ppm (s). ^{1}H NMR (C_6D_6, 400 MHz): 1.13 (s, CH_3); 1.72 (s, CH_2); 2.27 (s, CH_3); 2.45 (s, CH_2); 7.41 (m, CH). ν(C≡C) (Nujol) 2024 cm^{-1}. $M_w =$ 173,000 ($n_w = 279$).

[–Ru(DEPE)$_2$–C≡C-*p*-C_6H_4–C_6H_4-*p*-C≡C–]$_n$ (**14**). Yellow solid, 45% yield. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): 95.55 ppm (s). ν(C≡C) (CH_2Cl_2) 2047 cm^{-1}. Anal. Found C, 60.43; H, 8.34. $C_{36}H_{56}RuP_4$ calcd.: C, 60.43; H, 7.87%. $M_w = 28462$ ($n_w = 40$).

[–Ru(DEPE)$_2$–C≡C-*p*-C_6H_4–C≡C–]$_n$ (**15**). Yellow solid, 50% yield. ^{31}P{^{1}H} NMR ($CDCl_1$, 162 MHz): 95.54 ppm (s). ν(C≡C) (CH_2Cl_2) 2046 cm^{-1}. Anal. Found C, 56.84; H, 8.31. $C_{30}H_{52}RuP_4$ calcd.: C, 56.50; H, 8.22%. $M_w = 22468$ ($n_w = 35$).

[–Ru(DEPE)$_2$–C≡C-*p*-$C_6H_2(CH_3)_2$–C≡C–]$_n$ (**16**). Yellow solid, 55% yield. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): 95.52 ppm (s). ν(C≡C) (CH_2Cl_2) 2045 cm^{-1}. Anal. Found C, 57.89; H 8.34. $C_{32}H_{56}RuP_4$ calcd.: C, 57.73; H, 8.41%. $M_w = 28565$ ($n_w = 43$).

[–Os(DPPM)$_2$–C≡C-*p*-C_6H_4–C_6H_4-*p*-C≡C–]$_n$ (**17**). Orange solid, 60% yield. ν(C≡C) (Nujol) 2065 cm^{-1}. Anal. Found C, 68.64; H, 4.58. $C_{66}H_{52}OsP_4$ calcd.: C, 68.38; H, 4.52%.

[–Os(DPPM)$_2$–C≡C-*p*-$C_6H_2(CH_3)_2$–C≡C–]$_n$ (**19**). Light brown solid, 45% yield. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): 194.3 ppm (s). ν(C≡C) (CH_2Cl_2) 2054 cm^{-1}. Anal. Found C, 66.84; H, 4.17. $C_{62}H_{52}OsP_4$ calcd.: C, 67.01; H, 4.72%. $M_w = 18486$ ($n_w = 17$).

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