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Alkyne oligomerization mediated by rhodium complexes with a phosphinosulfonamido ligand and isolation and characterization of a rhodacyclopentadiene complex

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Abstract

Treatment of *N*-tosyl aziridine with $KPPh_2$ in THF produces $Ph_2PCH_2CH_2NTsK$ ($Ts = p\text{-}CH_3C_6H_4SO_2$). Reaction of $Ph_2PCH_2CH_2NTsK$ with $[Rh_2(\mu_2\text{-}Cl)_2(NBD)_2]$ (NBD = norbornadiene) and $[Rh_2(\mu_2\text{-}Cl)_2(COD)_2]$ (COD = 1,5-cyclooctadiene) produces [Rh(NBD)($Ph_2PCH_2CH_2NTs$)] and [Rh(COD)($Ph_2PCH_2CH_2NTs$)] (**4**), respectively. Reaction of $Ph_2PCH_2CH_2NTsK$ with $[Ir_2(\mu_2\text{-}Cl)_2(COD)_2]$ gives [Ir(COD)($Ph_2PCH_2CH_2NTs$)]. Complex **4** is catalytically active for polymerization of arylalkynes and for cyclotrimerization of HC≡CCOR (R = OEt, Me). The novel metallacycle [Rh(C(CO_2Et)=CHC(CO_2Et)=CH)(CH(CO_2Et)=CC≡CCO_2Et)($Ph_2PCH_2CH_2NHTs)_2$] was isolated from the reaction of **4** with ethyl propiolate. The metallacycle is catalytically active for cyclotrimerization of ethyl propiolate.

Keywords: Metallacycles; Oligomerization; Alkynes; N,P ligands; Rhodium; Iridium

1. Introduction

Phosphines are among the most popular ligands in coordination chemistry and catalysis. Sulfonamides RSO_2NHR', which can be readily deprotonated to give sulfonamido anions $[RSO_2NR]^-$ (much easier than deprotonation of RNHR′ to give $[RNR']^-$), have also attracted much recent attention in coordination chemistry and catalysis [1]. Thus it would be interesting to prepare metal complexes from phosphinosulfonamide ligands and to test their catalytic properties. However, well-characterized metal complexes prepared from phosphinosulfonamide ligands are very rare, although a few reports have appeared in the literature on the catalytic reactions mediated by Pd and Cu complexes with these ligands in the past few years [2]. It should be noted that the chemistry of late transition metal complexes with hard/soft chelating ligands has received much attention [3]. A number rhodium and iridium complexes with other P,N mixed-donor ligands (for example, phosphine-pyridine, phosphine-oxazoline, phosphine-pyrazolyl, and phosphine-imidazole) have been synthesized and investigated for their catalytic properties [4].

In this work, we have synthesized and characterized several new rhodium and iridium complexes with the phosphinosulfonamido ligand $[Ph_2PCH_2CH_2NTs]^-$ and investigated their catalytic properties for cyclotrimerization and polymerization of alkynes. During the course of the work, we have isolated a rhodacyclopentadiene complex from the reaction of [Rh(COD)($Ph_2PCH_2CH_2NTs$)] with HC≡CCO_2Et. In rhodium mediated catalytic cyclotrimerization reactions of alkynes [5], rhodacyclopentadienes have often been proposed as the intermediates. Although several rhodacyclopentadienes have been isolated from the reactions of rhodium complexes with internal alkynes [6], the isolation of rhodacyclopentadienes from the

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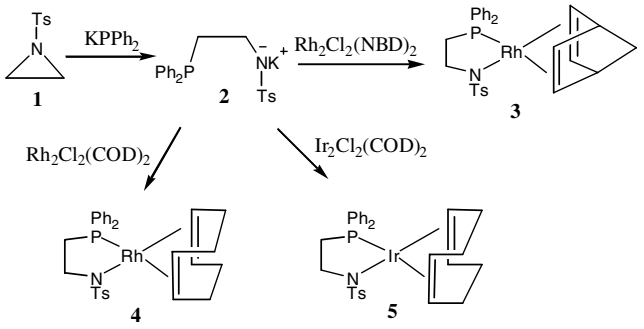
reactions of rhodium complexes with terminal alkynes is rare [7].

2. Results and discussion

2.1. Preparation of [M(diene)($Ph_2PCH_2CH_2NTs$)] complexes

Treatment of *N*-tosyl aziridine (**1**) [8] with $KPPh_2$ in THF produced the phosphinosulfonamido ligand $Ph_2PCH_2CH_2NTsK$ (**2**), which can be isolated as a white solid in 76% yield (Scheme 1). The compound has been characterized by NMR spectroscopy. In particular, the $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ showed a singlet at −21.5 ppm. The ^1H NMR spectrum in $CDCl_3$ showed the PCH_2 and NCH_2 signals at 2.79 and 2.04 ppm, in addition to the characteristic signals of Ts and PPh_2. Treatment of $Ph_2PCH_2CH_2NTsK$ with $[Rh_2(\mu_2\text{-}Cl)_2(NBD)_2]$ and $[Rh_2(\mu_2\text{-}Cl)_2(COD)_2]$ produced [Rh(NBD)($Ph_2PCH_2CH_2NTs$)] (**3**) and [Rh(COD)($Ph_2PCH_2CH_2NTs$)] (**4**), respectively. Similarly, reaction of $Ph_2PCH_2CH_2NTsK$ with $[Ir_2(\mu_2\text{-}Cl)_2(COD)_2]$ gave [Ir(COD)($Ph_2PCH_2CH_2NTs$)] (**5**). Reported complexes closely related to complexes **3**–**5** include amido complexes [Ir(COD)($Ph_2PCH_2CMe_2NH$)] [9], [Rh(COD)(2-pyridinecarboxamido)] [10], [M(CO)(PPh_3)($Ph_2PC_6H_4NH$)] (M = Rh, Ir) [11] and [Cp*RhCl(*N*-tolyl-1,2-cyclohexanediamine)] [12].

The structures of the new complexes can be readily assigned on the basis of their NMR and analytical data (see Section 3). In addition, the structure of **4** has also been confirmed by an X-ray diffraction study. The molecular structure of **4** is shown in Fig. 1. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively. The X-ray diffraction study confirms that the phosphinosulfonamido ligand is chelated to the rhodium center. The Rh–N bond distance (2.1310(18) Å) is similar to that in [Cp*RhCl(*N*-tolyl-1,2-cyclohexanediamine)] (2.152(7) Å) [12] and is slightly longer than that of [Rh(COD)(2-pyridinecarboxamido)] (2.007(4) Å) [10]. The C–C and C=C bond distances of the COD ligand and the Rh–C(olefin) distances are normal compared to those of the related Rh(COD) complex [Rh(COD)(2-pyridinecarboxamido)] [10].



Scheme 1.

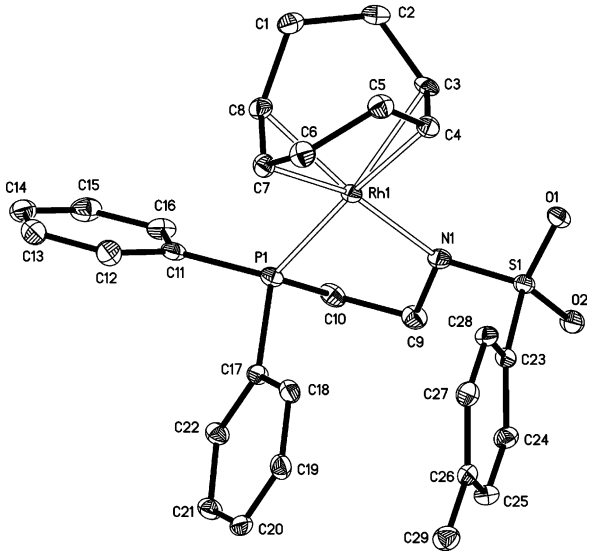


Fig. 1. The molecular structure of **4**. Selected bond distances (Å) and angles (°): Rh(1)–N(1), 2.1310(8); Rh(1)–P(1), 2.2606(6); Rh(1)–C(3), 2.229(2); Rh(1)–C(4), 2.264(2); Rh(1)–C(7), 2.117(2); Rh(1)–C(8), 2.138(2); P(1)–Rh(1)–N(1), 80.85(5).

2.2. Catalytic polymerization and cyclotrimerization reactions

Rhodium(I) complexes can initiate oligomerization or polymerization of alkynes depending on the ligand environments around rhodium, the structures of alkynes and the reaction conditions. Many Rh(diene) complexes, for example, [TpRh(COD)], $[Rh_2(\mu_2\text{-}Cl)_2(diene)_2]$/amine (diene = COD, NBD), $[Rh(COD)_2]BF_4$, [Rh(NBD)(η^6-$C_6H_5BPh_3$)], [Rh(C≡CPh)(NBD)(PPh_3)$_2$], [RhClL(COD)] (L = neutral phosphine or nitrogen donors), $[Rh(diene)(N\text{–}N)]^+$ (N–N = bidentate nitrogen donors) can catalyse alkyne polymerization [13]. Rhodium complexes such as $[Rh(COD)(binap)]^+$ (binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl), $[Rh_2(\mu_2\text{-}Cl)_2(COD)_2]$/TPPTS (TPPTS = tris(3-sulfonatophenyl)phosphine) and $[RhCl(PPh_3)_3]$ can promote catalytic cyclotrimerization of alkynes [5]. In this work, we have studied the reactivity of complexes **4** and [Rh(NBD)($Ph_2PCH_2CH_2NTs$)] towards terminal alkynes, in order to see how the phosphinosulfonamido ligand $[Ph_2PCH_2CH_2NTs]^-$ might influence the reactivity or catalytic activity of the rhodium center.

Complex **4** was found to be catalytically active for polymerization of arylalkynes (Eq. (1)). As shown in Table 4, phenylacetylene is polymerized in organic solvents such as $CDCl_3$, CH_2Cl_2, benzene and THF (entries 1–5) to give polymers with molecular weights (M_w) in the range of 17 800–63 200 and polydispersities in the range of 1.55–2.88. The yields of the polymerization reactions carried out in THF are better than those in $CDCl_3$, CH_2Cl_2 or benzene, although the origin of the difference is not clear to us. For comparison, the molecular weight (M_w) and polydispersity of poly(phenylacetylene) obtained with $[Tp^{Ph,Me}Rh(COD)]$ in CH_2Cl_2 are 47 000 and 2.38,

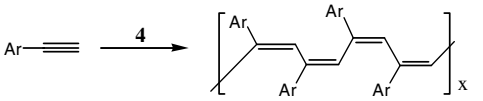
Table 1
Crystal data and structure refinement for **4** and **8**

Compound	**4**	**8**
Formula	$C_{29}H_{33}NO_2PRhS$	$C_{62}H_{67}N_2O_{12}P_2RhS_2$
Formula weight	593.50	1261.15
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$I2/a$
a (Å)	13.4721(7)	30.166(3)
b (Å)	13.2768(7)	11.2074(11)
c (Å)	15.7838(9)	37.312(4)
β (°)	113.3660(10)	109.793(2)
Volume (Å^3)	2591.7(2)	11869(2)
Z	4	8
D_{calcd} (g/cm^3)	1.521	1.411
Absorption coefficient (mm^{-1})	0.829	0.476
θ Range (°)	1.69–26.00	1.43–25.00
Index ranges	$-14 \leqslant h \leqslant 16$, $-16 \leqslant k \leqslant 16$, $-19 \leqslant l \leqslant 19$	$-35 \leqslant h \leqslant 35$, $-13 \leqslant k \leqslant 9$, $-44 \leqslant l \leqslant 37$
Number of reflections collected	13611	29409
Number of independent reflections [R_{int}]	5023 [0.0309]	10398 [0.1140]
Maximum and minimum transmission	1.00 and 0.82	1.00 and 0.69
Number of data/ restraints/parameters	5023/0/316	10398/0/732
Goodness-of-fit on F^2	1.018	1.002
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0298$, $wR_2 = 0.0721$	$R_1 = 0.0576$, $wR_2 = 0.0969$
Largest difference peak and hole (e Å^{-3})	0.768 and −0.594	1.581 and −0.908

Table 2
Selected bond lengths (Å) and angles (°) for **4**

Rh(1)–N(1)	2.1310(18)	Rh(1)–P(1)	2.2605(6)
Rh(1)–C(3)	2.229(2)	Rh(1)–C(4)	2.264(2)
Rh(1)–C(7)	2.117(2)	Rh(1)–C(8)	2.138(2)
C(3)–C(4)	1.366(3)	C(7)–C(8)	1.405(3)
N(1)–Rh(1)–P(1)	80.85(5)	C(8)–Rh(1)–P(1)	95.52(6)
C(3)–Rh(1)–C(4)	35.38(8)	C(7)–Rh(1)–C(8)	38.57(9)
C(7)–Rh(1)–C(4)	80.35(9)	C(8)–Rh(1)–C(3)	80.41(8)
C(3)–Rh(1)–P(1)	156.15(6)	P(1)–Rh(1)–C(4)	168.47(6)
C(7)–Rh(1)–P(1)	94.19(6)	N(1)–Rh(1)–C(8)	160.91(8)
C(7)–Rh(1)–N(1)	159.73(8)	N(1)–Rh(1)–C(4)	100.77(8)
N(1)–Rh(1)–C(3)	95.30(7)	C(7)–Rh(1)–C(3)	96.83(9)
C(8)–Rh(1)–C(4)	86.55(8)	C(9)–N(1)–Rh(1)	119.28(14)
C(10)–P(1)–Rh(1)	100.47(8)	S(1)–N(1)–Rh(1)	124.52(10)
C(3)–C(4)–Rh(1)	70.92(13)	C(4)–C(3)–Rh(1)	73.70(13)
C(8)–C(7)–Rh(1)	71.55(12)	C(7)–C(8)–Rh(1)	69.87(12)
C(1)–C(8)–Rh(1)	114.08(15)	C(6)–C(7)–Rh(1)	110.10(15)
C(2)–C(3)–Rh(1)	107.34(14)	C(5)–C(4)–Rh(1)	110.73(15)
C(11)–P(1)–Rh(1)	124.05(7)	C(17)–P(1)–Rh(1)	115.66(7)

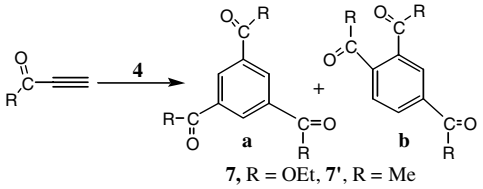
respectively [13a]; and those with [Rh(C≡CPh)(NBD)-(PPh$_3$)$_2$] in THF are 9010 and 1.17, respectively [6c]. As indicated by the ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data, the poly(phenylacetylene) formed from the reaction mainly has a *cis*-transoidal structure [13g]. Preferential formation of *cis*-transoidal poly(phenylaceylene) is common with Rh(I) catalysts [13]. Complex **4** is also catalytically active for the polymerization of *p*-tolylacetylene (entry 6) to give poly(*p*-tolylacetylene) with a similar structure. As indicated by an in situ NMR experiment, complex **3** is also catalytically active for polymerization of phenylacetylene, giving poly(phenylacetylene) with properties similar to those obtained with complex **4**. It is known that rhodium complex [Rh(C≡CPh)(NBD)(PPh$_3$)$_2$] can polymerize phenylacetylene to give living polymer, which can initiate further polymerization of alkynes [6c]. In our case, the isolated polymers do not appear to have active rhodium centers, as they do not react with additional phenylacetylene or *p*-tolylacetylene in THF.



6a, R = Ph; **6b**, R = p-tolyl (1)

There are strong evidences that rhodium(I) mediated polymerization of arylalkynes proceeds through insertion of alkyne to Rh–vinyl bond [6c]. We assume that similar mechanism is also involved in our system. Unfortunately, our attempt to observe the reaction intermediates in the reaction of complex **4** with HC≡CPh failed. When the reaction of complex **4** with HC≡CPh in CD_2Cl_2 was monitored by ^{31}P NMR spectroscopy, only the ^{31}P signals of complex **4** and phosphine oxide can be observed.

Like many other Rh(I) complexes [13], complex **4** is catalytically active for polymerization of arylalkynes, but has very low catalytic activity, if any, for polymerization of aliphatic alkynes such as *t*-BuC≡CH and *n*-BuC≡CH. Interestingly, when activating alkynes such as HC≡CCO$_2$Et and HC≡CCOMe were used as the substrates, they were mainly converted to the cyclotrimers 1,3,5- and 1,2,4-C$_6$H$_3$(COR)$_3$ (**7**, R = OEt; **7′**, R = Me) in a ratio of ca. 1.1 rather than polymers (Eq. (2)). Cyclotrimerization of HC≡CCO$_2$Et in benzene occurred at room temperature in the presence of 3.3 mol% or 0.40 mol% of complex **4**. The Rh/substrate ratio, although affects the reaction rate, has negligible effect on the distribution of the two isomeric products. We have also carried out competitive reaction between HC≡CCO$_2$Et and PhC≡CH. In the presence of 1 mol% complex **4**, a 1:1 mixture of HC≡CCO$_2$Et and PhC≡CH is converted to a complicated mixture, as indicated by in situ ^{1}H NMR. The mass spectrum of the organic product obtained after purification by column chromatography showed ion peaks corresponding to C$_6$H$_3$(CO$_2$Et)$_3$ (3HC≡CCO$_2$Et), C$_6$H$_3$(Ph)(CO$_2$Et)$_2$-(HC≡CPh + 2HC≡CCO$_2$Et), and C$_6$H$_3$(Ph)$_2$(CO$_2$Et)-(2HC≡CPh + HC≡CCO$_2$Et), suggesting that cyclotrimerization of HC≡CCO$_2$Et and co-cyclotrimerization of HC≡CPh and HC≡CCO$_2$Et occurred. In agreement with the MS, the ^{1}H NMR spectrum showed the characteristic proton signals of 1,3,5- and 1,2,4-C$_6$H$_3$(CO$_2$Et)$_3$ along with additional proton signals in the region 7.2–8.8 ppm. Unfortunately, we have not been able to fully separate and characterize by NMR the co-cyclotrimerized species C$_6$H$_3$(Ph)(CO$_2$Et)$_2$ and C$_6$H$_3$(Ph)$_2$(CO$_2$Et).

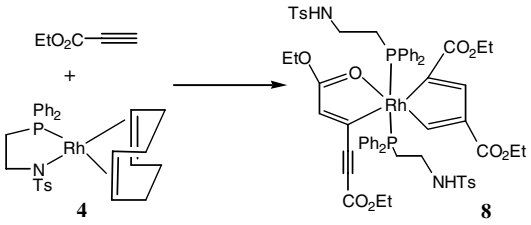


(2)

In contrast, the iridium complex **5** did not initiate either polymerization or oligomerization of phenylacetylene and ethyl propiolate under similar conditions. It should be noted that alkyne polymerization or cyclotrimerization mediated by iridium complexes is known. For example, complexes such as $[HIr(COD)(PR_3)_2]$, $[Ir_2(\mu_2\text{-}X)_2(COD)_2]$ (X = Cl, OMe) and $Ir_2(\mu_2\text{-}Cl)_2(COD)_2/Ph_2C=CPhLi$ can catalyze the polymerization of phenylacetylene [14]; complexes such as [HIr(COD)(dppe)] and $[Ir_2(\mu_2\text{-}Cl)_2(COD)_2]/P(C_6F_5)_2CH_2CH_2P(C_6F5)_2$ can catalyze the cyclotrimerization of alkynes [15].

2.3. Isolation of the metallacycle *8*

We have tried to detect the reaction intermediates in the reaction of complex **4** with $HC{\equiv}CCO_2Et$. When the reaction of complex **4** with $HC{\equiv}CCO_2Et$ in CD_2Cl_2 was monitored by ^{31}P NMR spectroscopy, it was observed that the ^{31}P signals of complex **4** gradually disappeared, and a doublet at 17.4 ppm gradually appeared as the major new ^{31}P signals. The relative amount of $HC{\equiv}CCO_2Et$ do not appear to have much effect on the course of the reaction, but a larger excess of $HC{\equiv}CCO_2Et$ can speed up the consumption of complex **4** and the formation of **8**. The new major species can be isolated as a yellow solid and was identified to be the metallacycle $[Rh(C(CO_2Et){=}CHC(CO_2Et){=}CH)(CH(CO_2Et){=}CC{\equiv}CCO_2Et)(Ph_2PCH_2CH_2NHTs)_2]$ (**8**) (Eq. (3)). The other minor phosphorus-containing species produced from the reaction, however, are difficult to be isolated and characterized.



(3)

The structure of the metallacycle has been confirmed by X-ray diffraction. The molecular structure is shown in Fig. 2 and selected bond distances and angles are given in Table 3. The crystal structure reveals that four molecules of $HC{\equiv}CCO_2Et$ have been incorporated into the rhodium center: two of them are joined together with the metal center to form a metallacyclopentadiene ring, and the other two coupled to form a $CH(CO_2Et){=}CC{\equiv}CCO_2Et$ ligand which is also chelated to rhodium. The coordination geometry around rhodium can be described as a distorted octahedron with the PPh_2 groups *trans* to each other. The rhodacyclopentadiene ring is nearly planar with mean plane deviation of 0.02 Å. In the metallacycle, the C(80)–C(72) (1.358(7) Å) and C(73)–C(74) (1.359(6) Å) bonds are slightly shorter than that of C(72)–C(73) (1.455(6) Å),

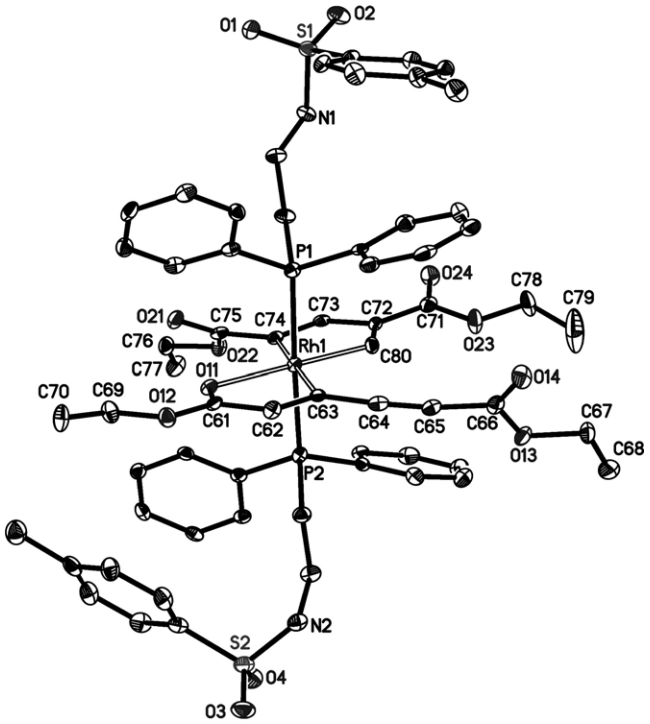


Fig. 2. The molecular structure of **8**. Selected bond distances (Å) and angles (°): Rh(1)–P(1), 2.3218(14); Rh(1)–P(2), 2.3243(14); Rh(1)–C(63), 2.089(5); Rh(1)–O(11), 2.223(3); Rh(1)–C(74), 2.098(5); Rh(1)–C(80), 1.972(4); O(11)–C(61), 1.246(5); C(61)–C(62),1.444(6); C(62)–C(63), 1.350(6); C(72)–C(80), 1.358(7); C(72)–C(73), 1.455(6); C(73)–C(74), 1.359(6); P(1)–Rh(1)–P(2), 174.53(5); C(63)–Rh(1)–O(11), 75.95(15); C(74)–Rh(1)–C(80), 79.18(19).

Table 3
Selected bond lengths (Å) and angles (°) for **8**

Rh(1)–C(80)	1.972(4)	Rh(1)–C(74)	2.098(5)
Rh(1)–C(63)	2.089(5)	Rh(1)–O(11)	2.223(3)
Rh(1)–P(1)	2.3218(14)	Rh(1)–P(2)	2.3243(14)
C(61)–C(62)	1.444(6)	C(62)–C(63)	1.350(6)
C(72)–C(80)	1.358(7)	C(72)–C(73)	1.455(6)
C(73)–C(74)	1.359(6)	O(11)–C(61)	1.246(5)
O(21)–C(75)	1.229(5)	O(24)–C(71)	1.203(6)
C(80)–Rh(1)–C(63)	98.8(2)	C(80)–Rh(1)–C(74)	79.18(19)
C(80)–Rh(1)–O(11)	174.46(17)	C(80)–Rh(1)–P(1)	84.23(14)
C(80)–Rh(1)–P(2)	91.96(14)	C(63)–Rh(1)–C(74)	177.41(19)
C(63)–Rh(1)–O(11)	75.95(15)	C(63)–Rh(1)–P(1)	91.94(13)
C(63)–Rh(1)–P(2)	92.52(13)	C(74)–Rh(1)–O(11)	106.09(15)
C(74)–Rh(1)–P(1)	89.52(13)	C(74)–Rh(1)–P(2)	85.91(13)
O(11)–Rh(1)–P(1)	93.99(9)	O(11)–Rh(1)–P(2)	90.17(9)
P(1)–Rh(1)–P(2)	174.53(5)	C(61)–O(11)–Rh(1)	111.8(3)
C(7)–P(1)–Rh(1)	117.66(16)	C(27)–P(2)–Rh(1)	114.31(16)
C(62)–C(63)–Rh(1)	116.3(3)	C(64)–C(63)–Rh(1)	121.3(3)
C(75)–C(74)–Rh(1)	126.9(3)	C(72)–C(80)–Rh(1)	118.2(4)
C(73)–C(74)–Rh(1)	112.9(3)	C(62)–C(63)–C(64)	122.2(5)
C(63)–C(62)–C(61)	114.2(5)	C(65)–C(64)–C(63)	171.6(5)
C(64)–C(65)–C(66)	173.2(5)	C(80)–C(72)–C(73)	113.9(4)
C(80)–C(72)–C(71)	124.0(5)	C(73)–C(72)–C(71)	122.1(5)
C(74)–C(73)–C(72)	115.8(5)	C(73)–C(74)–C(75)	120.1 (5)

as one might expect for a metallacyclopentadiene ring. The structural features of the five-membered metallacyle are similar to other structurally characterized rhodacyclopentadienes. The bond distances associated with the Rh(η^2-C(C≡CCO_2Et)=$CHCO_2$Et) are comparable to those reported for the related complexes [(η^5:η^1-(3-NIM)Ind-P)Rh(η^2-CPh=CMeCMe=O)] ((3-NIM)Ind-P, a phosphorus-containing indenyl ligand) [16] and [Cp*RhCl-(μ-SPr)(μ-S(*i*-Pr)C=$CHCO_2$Me)RhCp*]OTf [17]. The solid-state structure is supported by the NMR spectroscopic data. In particular, the $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 showed a doublet at 17.4 ppm (J(RhP) = 110.6 Hz). The ^1H NMR spectrum in C_6D_6 showed four sets of OEt proton signals, the RhC*H* signal at 9.67 ppm, the C*H*(CO_2Et) signal at 6.60 ppm, and the C*H*=C(Rh)CO_2Et signal at 8.35 ppm. A good $^{13}C\{^1H\}$ NMR spectrum could not be obtained due to its poor solubility in common organic solvents.

One may ask how complex **8** was formed. The fact that the starting material **4** has only one phosphine ligand and that complex **8** contains two phosphine ligands suggests that formation of **8** is not a simple process and that there must be other species generated along with **8**. Unfortunately, we have not been able to identify any complexes except **8** from the reaction. Thus the detailed mechanism for the formation of **8** cannot be defined. Intuitively, the rhodacyclopentadiene fragment Rh(C(CO_2Et)=CH–C(CO_2Et)=CH) can be formed by oxidative coupling of two molecules of HC≡CCO_2Et on rhodium, and the vinyl fragment Rh(C(C≡CCO_2Et)=$CHCO_2$Et) could be formed by coupling the acetylide and vinylidene ligands of an intermediate containing Rh(C≡CCO_2Et)(=C=$CHCO_2$Et). Reactions of Rh(I) complexes with terminal alkynes to give vinylidene complexes are well known [18]. Intramolecular coupling reactions between acetylide and vinylidene ligands on rhodium have also been demonstrated [19].

Complex **8** represents a rare example of rhodacyclopentadiene formed from oxidative coupling of two molecules of a terminal alkyne on rhodium. Rhodacyclopentadienes are interesting because they have often been proposed as the intermediates for cyclotrimerization of alkynes mediated by rhodium complexes. Until now, only a few of such complexes have been isolated from the reactions of alkynes with rhodium complexes [6,7], although there are many reported examples of alkyne cyclotrimerization using Rh complexes as the catalysts [5]. Most of the reported rhodacyclopentadienes are generated from coupling of internal alkynes [6]. A previous example of rhodacyclopentadiene formed from coupling of terminal alkyne on rhodium is reported by Bianchini et al. from the reaction of [RhCl(C_2H_4)CH_3(C(CH_2PPh_2)$_3$)] with HC≡CH [7].

2.4. Catalytic activity of complex *8*

We have also tested the catalytic activity of the metallacycle **8** for polymerization and trimerization of alkynes. Complex **8** was found to initiate the cyclotrimerization of HC≡CCO_2Et. Thus, when a benzene solution of HC≡CCO_2Et containing **8** (8 mol%) was heated at 50 °C, ca. 64% of HC≡CCO_2Et was converted cleanly to a mixture of **7a** and **7b** in a ratio of 1:1. However, no reaction was observed when **8** is mixed with PhC≡CH even under refluxing conditions. When the reaction of **8** with HC≡CCO_2Et or HC≡CPh was monitored by $^{31}P\{^1H\}$ NMR, only the ^{31}P signal of **8** can been seen.

3. Experimental

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, ether, THF), sodium (benzene), or calcium hydride (CH_2Cl_2). The starting materials tosyl aziridine [8], [Rh_2(μ$_2$-Cl)$_2$(COD)$_2$] [20], [Rh_2(μ$_2$-Cl)$_2$-(NBD)$_2$] [21] and [Ir_2(μ$_2$-Cl)$_2$(COD)$_2$] [22] were prepared according to the literature methods. All other reagents were used as purchased from Aldrich Chemical Co., USA.

Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were collected on a Bruker ARX-300 spectrometer (300 MHz). ^1H and ^{13}C NMR shifts are relative to TMS, and ^{31}P chemical shifts relative to 85% H_3PO_4. The molecular weights and molecular weight distribution (M_w/M_n) of polymers were measured by a Waters Associates 510 GPC using THF as the eluent and were calibrated with polystyrene standards.

3.1. $Ph_2PCH_2CH_2NTsK$ (*2*)

To a THF solution of $KPPh_2$ (12.0 mL, 0.5 M, 6.00 mmol) was added dropwise a solution of tosyl aziridine (1.13 g, 5.75 mmol) in THF (40 mL) at 0 °C (the addition was completed in 1 h). The reaction mixture was then allowed to warm up to r.t. and stirred overnight. The mixture was filtered and the filtrate was concentrated to dryness under vacuum. The residue was washed with diethyl ether (20 mL × 3) and hexane (10 mL) and dried under vacuum to give a white solid. The solid was extracted with MeOH (30 mL) and then filtered to give a clear colorless solution. The MeOH was removed under vacuum to give a white solid, which was collected by filtration, washed with ether, and dried under vacuum. Yield: 1.84 g, 76%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 298 K): δ −21.5 (s). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.04 (t, $J_{H,H}$ = 7.2 Hz, 2H, CH_2N), 2.21 (s, 3H, CH_3), 2.79 (dt, $J_{P,H}$ = 10.1 Hz, $J_{H,H}$ = 7.2 Hz, 2H, CH_2P), 6.85 (d, $J_{H,H}$ = 8.1 Hz, 2H, Ph of Ts), 7.10–7.21 (m, 10H, PPh_2), 7.49 (d, $J_{H,H}$ = 8.1 Hz, 2H, Ph of Ts).

3.2. [*Rh*(*COD*)(*Ph*$_2$*PCH*$_2$*CH*$_2$*NTs*)] (*4*)

To a stirred solution of [Rh_2(μ$_2$-Cl)$_2$(COD)$_2$] (0.208 g, 0.422 mmol) in THF (30 mL) was added a solution of

$PPh_2CH_2CH_2NTsK$ (0.355 g, 0.842 mmol) in THF (30 mL) at 0 °C. After the addition was completed, the resulting mixture was stirred for further 30 min at 0 °C, and then warmed up to room temperature. The reaction mixture was filtered, and the filtrate was concentrated to dryness under vacuum. The residue was washed with diethyl ether (5 mL × 3) to give a yellow powder. The analytically pure sample of **4** was obtained by column chromatography on alumina with MeOH–THF (1:2, v/v) as the eluent. Yield: 0.343 g, 69%. IR (KBr pellet, cm^{-1}): $\nu_{asym}(SO_2)$ 1279, $\nu_{sym}(SO_2)$ 1138. ^{31}P $\{^1H\}$ NMR (121.5 MHz, C_6D_6, 298 K): δ 50.0 (d, $J_{Rh,P} = 179.5$ Hz). ^1H NMR (300 MHz, C_6D_6, 298 K): δ 1.99–2.15 (m, 6H, CH_2), 2.26 (s, 3H, CH_3), 2.33–2.44 (m, 4H, CH_2P, CH_2), 3.29 (br s, 2H, =CH), 3.54 (dt, $J_{P,H} = 27.7$ Hz, $J_{H,H} = 6.1$ Hz, 2H, CH_2N), 7.17–7.27 (m, 10H, =CH, Ph of Ts, PPh_2), 7.57 (t, $J_{H,H} = 8.4$ Hz, 4H, PPh_2), 8.44 (d, $J_{H,H} = 8.0$ Hz, 2H, Ts). ^{13}C $\{^1H\}$ NMR (75.5 MHz, C_6D_6, 298 K): δ 21.6 (s, CH_3), 29.6 (s, CH_2 of COD), 32.1 (d, $J_{P,C} = 27.0$ Hz, PCH_2), 33.5 (d, $J_{P,C} = 2.9$ Hz, CH_2 of COD), 48.9 (d, $J_{P,C} = 5.4$ Hz, CH_2N), 67.8 (d, $J_{Rh,C} = 12.8$ Hz, =CH), 110.0 (dd, $J_{Rh,C} = 10.1$ Hz, $J_{P,C} = 6.4$ Hz, =CH), 128.1 (s, C_6H_4), 129.3 (d, $J_{P,C} = 9.7$ Hz, *o*- or *m*-PPh_2), 129.5 (s, C_6H_4), 131.1 (d, $J_{P,C} = 2.2$ Hz, *p*-PPh_2), 132.0 (dd, $J_{P,C} = 41.8$ Hz, $J_{Rh,C} = 5.3$ Hz, *ipso*-PPh_2), 133.7 (d, $J_{P,C} = 10.8$ Hz, *o*- or *m*-PPh_2), 140.2 (s, C of C_6H_4), 144.1 (s, C of C_6H_4). Anal. Calc. for $C_{29}H_{33}NO_2PRhS$ (593.52): C, 58.69; H, 5.60; N, 2.36. Found: C, 58.50; H, 5.52; N, 2.30%.

3.3. *[Rh(NBD)(Ph2PCH2CH2NTs)] (3)*

To a stirred solution of $[Rh_2(\mu_2\text{-}Cl)_2(NBD)_2]$ (0.053 g, 0.12 mmol) in THF (8 mL) was added a solution of $PPh_2CH_2CH_2NTsK$ (0.097 g, 0.23 mmol) in THF (8 mL) at 0 °C. After the addition was completed, the resulting mixture was stirred for further 40 min at 0 °C, and then warmed up to room temperature. The reaction mixture was filtered, the filtrate was concentrated to dryness under vacuum. The residue was extracted with benzene (5 mL). The benzene was removed to give a yellow solid, which was collected by filtration, washed with diethyl ether (3 mL × 2) and dried under vacuum to give a yellow powder. Yield: 0.080 g, 60%. IR (KBr pellet, cm^{-1}): $\nu_{asym}(SO_2)$ 1289, $\nu_{sym}(SO_2)$ 1141. ^{31}P $\{^1H\}$ NMR (121.5 MHz, C_6D_6, 298 K): δ 50.0 (d, $J_{Rh,P} = 180.3$ Hz). ^1H NMR (300 MHz, C_6D_6, 298 K): δ 1.48 (t, $J_{H,H} = 1.2$ Hz, 2H, CH_2 of NBD), 2.04 (m, 2H, CH_2P), 2.25 (s, 3H, CH_3), 3.37 (br m, 2H, bridge-head CH of NBD), 3.51 (dt, $J_{P,H} = 26.7$ Hz, $J_{H,H} = 6.0$ Hz, 2H, CH_2N), 3.64 (br s, 2H, =CH), 6.59 (br s, 2H, =CH), 7.19–7.28 (m, 8H, PPh_2, Ph of Ts), 7.45–7.52 (m, 4H, PPh_2), 8.46 (d, $J_{H,H} = 8.1$ Hz, 2H, Ph of Ts). ^{13}C $\{^1H\}$ NMR (75.5 MHz, C_6D_6, 298 K): δ 20.9 (s, CH_3), 32.5 (d, $J_{P,C} = 26.8$ Hz, CH_2P), 48.0 (d, $J_{P,C} = 5.4$ Hz, CH_2N), 49.4 (d, $J_{Rh,C} = 10.9$ Hz, CH of NBD), 51.0 (s, =CH), 65.2 (d, $J_{Rh,C} = 4.6$ Hz, CH_2 of NBD), 94.2 (dd, $J_{P,C} = 4.9$ Hz, $J_{Rh,C} = 9.9$ Hz, =CH of NBD), 127.5 (s, C_6H_4), 128.7 (d, $J_{P,C} = 9.9$ Hz, *o*- or *m*-PPh_2), 128.9 (s, C_6H_4), 130.2 (d, $J_{P,C} = 2.0$ Hz, *p*-PPh_2), 130.6, 131.2 (dd, $J_{P,C} = 41.6$ Hz, $J_{Rh,C} = 3.1$ Hz, *ipso*-PPh_2), 132.6 (d, $J_{P,C} = 11.5$ Hz, *o*- or *m*-PPh_2), 139.6 (s, C of C_6H_4), 143.9 (s, C of C_6H_4). Anal. Calc. for $C_{28}H_{29}NO_2PRhS$ (577.48): C, 58.24; H, 5.06; N, 2.43. Found: C, 57.99; H, 5.16; N, 2.38%.

3.4. *[Ir(COD)(Ph2PCH2CH2NTs)] (5)*

To a stirred solution of $[Ir_2(\mu_2\text{-}Cl)_2(COD)_2]$ (0.205 g, 0.305 mmol) in THF (10 mL) was added a solution of $PPh_2CH_2CH_2NTsK$ (0.258 g, 0.612 mmol) in THF (15 mL) at 0 °C. After the addition was completed, the resulting mixture was stirred for further 60 min at 0 °C, and then warmed up to room temperature. The reaction mixture was filtered, the filtrate was concentrated under vacuum to give a red oil, to which was added ether (5 mL) to produce a yellowish orange solid. The solid was collected by filtration, washed with diethyl ether (5 mL × 2) to give a yellow powder. An analytically pure sample of **5** was obtained by column chromatography on alumina with ether/THF (5:2.5–3, v/v) as the eluent. Yield: 0.308 g, 74%. IR (KBr pellet, cm^{-1}): $\nu_{asym}(SO_2)$ 1279, $\nu_{sym}(SO_2)$ 1138. ^{31}P $\{^1H\}$ NMR (121.5 MHz, C_6D_6, 298 K): δ 39.0 (s). ^1H NMR (300 MHz, C_6D_6, 298 K): δ 1.80–1.88 (m, 2H, CH_2 of COD), 1.97–2.04 (m, 4H, CH_2 of COD), 2.23 (s, 3H, CH_3), 2.25–2.37 (m, 4H, CH_2 of COD and CH_2P), 2.89 (br m, 2H, =CH), 3.66 (dt, $J_{P,H} = 26.0$, $J_{H,H} = 6.1$ Hz, 2H, CH_2N), 6.95 (br m, 2H, =CH), 7.15 (d, $J_{H,H} = 7.8$ Hz, 2H, Ph of Ts), 7.19–7.23 (m, 6H, PPh_2), 7.57 (m, 4H, PPh_2), 8.44 (d, $J_{H,H} = 7.8$ Hz, 2H, Ph of Ts). ^{13}C $\{^1H\}$ NMR (75.5 MHz, C_6D_6, 298 K): δ 21.6 (s, CH_3), 30.9 (s, CH_2 of COD), 33.4 (d, $J_{P,C} = 3.7$ Hz, $CH_2$of COD), 33.5 (d, $J_{P,C} = 31.5$ Hz, PCH_2), 50.7 (s, =CH), 52.7 (d, $J_{P,C} = 4.2$ Hz, NCH_2), 99.3 (d, $J_{P,C} = 12.2$ Hz, =CH), 128.1 (s, C_6H_4), 129.2 (d, $J_{P,C} = 10.1$ Hz, *o*- or *m*-PPh_2), 129.6 (s, C_6H_4), 130.8 (d, $J_{P,C} = 50.3$ Hz, *ipso*-PPh_2), 131.3 (d, $J_{P,C} = 2.3$ Hz, *p*-PPh_2), 134.0 (d, $J_{P,C} = 10.6$ Hz, *o*- or *m*-PPh_2), 140.8 (s, C of C_6H_4), 143.3 (s, C of C_6H_4). Anal. Calc. for $C_{29}H_{33}IrNO_2PS$ (682.83): C, 51.01; H, 4.87; N, 2.05. Found: C, 51.15; H, 4.73; N, 2.03%.

3.5. *Cyclotrimerization of ethyl propiolate and isolation of [Rh(C(CO2Et)=CHC(CO2Et)=CH)(CH(CO2Et)=CC≡CCO2Et)(Ph2PCH2CH2NHTs)] (8)*

A mixture of complex **4** (1.004 g, 1.629 mmol) and ethyl propiolate (4.90 mL, 48.4 mmol) in dichloromethane (35 mL) was stirred for 3.5 h. The volatile materials were then removed under vacuum, the resulting residue was extracted with benzene (20 mL, 5 mL × 2), and the combined extracts were concentrated to dryness. Column chromatography on alumina (deactivated with 1% H_2O, v/v) with dichloromethane as the eluent gave a mixture of cyclotrimers 1,2,4- and 1,3,5-benzenetricarboxylic acid in a

molar ratio of 1.1:1. Yield: 1.95 g, 41% (based on ethyl propiolate). Pure 1,3,5-isomer can be obtained as a white solid, when the mixture was washed with acetone. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) data of 1,2,4-$C_6H_3(CO_2Et)_3$: δ 1.33 (t, $J_{H,H} = 7.2$ Hz, 9H, CH_3), 4.35 (q, $J_{H,H} = 7.2$ Hz, 6H, OCH_2), 7.73 (d, $J_{H,H} = 8.0$ Hz, 1H, Ph), 8.16 (dd, $J_{H,H} = 8.0$ Hz, $J_{H,H} = 1.5$ Hz, 1H, Ph), 8.37 (d, $J_{H,H} = 1.5$ Hz, 1H, Ph). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) data of 1,3,5-$C_6H_3(CO_2Et)_3$: δ 1.43 (t, $J_{H,H} = 7.1$ Hz, 9H, CH_3), 4.44 (q, $J_{H,H} = 7.1$ Hz, 6H, OCH_2), 8.85 (s, 3H, Ph). Further eluting with THF gave a red syrup after the solvent was evaporated, which was chromatographed twice on silica with MeOH/dichloromethane (1:100, v/v) as the eluent to give complex **8** as a red solid, which was purified by recrystallization from benzene to give yellow crystals. Yield: 180 mg, 17% (based on the rhodium complex). Characterization data of **8**: ^{31}P {^{1}H} NMR (121.5 MHz, C_6D_6, 298 K): δ 17.4 (d, $J_{Rh,P} = 110.6$ Hz). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.06 (t, $J_{H,H} = 7.1$ Hz, 3H, CH_3), 1.26 (t, $J_{H,H} = 7.1$ Hz, 3H, CH_3), 1.40 (t, $J_{H,H} = 7.1$ Hz, 3H, CH_3), 1.57 (t, $J_{H,H} = 7.1$ Hz, 3H, CH_3), 2.14 (s, 6H, CH_3), 2.8–3.0 (m, 8H, PCH_2CH_2N), 3.87 (q, $J_{H,H} = 7.1$ Hz, 2H, OCH_2), 4.24 (q, $J_{H,H} = 7.1$ Hz, 2H, OCH_2), 4.36 (q, $J_{H,H} = 7.1$ Hz, 2H, OCH_2), 4.69 (q, $J_{H,H} = 7.1$ Hz, 2H, OCH_2), 5.70 (br t, 2H, NH), 6.60 (br, 1H, =CH), 7.03 (d, $J_{H,H} = 8.1$ Hz, 4H, Ph of Ts), 7.17–7.24 (m, 4H, PPh_2), 7.32–7.43 (m, 8H, PPh_2), 7.74 (m, 8H, PPh_2), 7.85 (d, $J_{H,H} = 8.1$ Hz, 4H, Ph of Ts), 8.35 (br s, 1H, RhC(CO_2Et)=C*H*), 9.67 (br, 1H, RhCH). Anal. Calc. for $C_{62}H_{67}N_2O_{12}P_2RhS_2$-(1261.18): C, 59.04; H, 5.35; N, 2.22. Found: C, 59.31; H, 5.49; N, 2.25%.

3.6. Cyclotrimerization of HC≡CCOMe

A mixture of complex **4** (8.9 mg, 0.015 mmol) and HC≡CCOMe (0.116 mL, 1.50 mmol) in THF (5 mL) was stirred at r.t. for 20 h. The reaction mixture was concentrated under reduced pressure. The product was purified by column chromatography on silica gel eluting with dichloromethane and dichloromethane/acetone (20:3, v/v) to give a pale yellow needles after removal of solvents. The product is a mixture of 1,3,5-$C_6H_3(COMe)_3$ and 1,2,4-$C_6H_3(COMe)_3$ in a ratio of 1:1. Yield: 20 mg, 20%. ^{1}H NMR of 1,3,5-$C_6H_3(COMe)_3$ (300 MHz, $CDCl_3$, 298 K): δ 2.71 (s, 9H, CH_3), 8.70 (s, 3H, Ph). ^{1}H NMR of 1,2,4-$C_6H_3(COMe)_3$(300 MHz, $CDCl_3$, 298 K): δ 2.55 (s, 3H, CH_3), 2.61 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 7.58 (d, $J(HH) = 7.9$ Hz, 1H, Ph), 8.11 (dd, $J(HH) = 1.5$ Hz, 7.9 Hz, 1H, Ph), 8.20 (d, $J(HH) = 1.5$ Hz, 1H, Ph). MS (CI, exact mass, 204.08, *m*/*z*): 205 (M + 1).

3.7. Cyclotrimerization of HC≡CCO$_2$Et in the presence of PhC≡CH

A mixture of complex **4** (17.8 mg, 0.0300 mmol), HC≡CCO_2Et (0.152 mL, 1.50 mmol) and PhC≡CH (0.165 mL, 1.50 mmol) in THF (5 mL) was stirred at r.t. for 20 h. The mixture was then concentrated under reduced pressure. The product was purified by column chromatography on silica eluting with dichloromethane to give a pasty mixture of $C_6H_3(COOEt)_3$, $C_6H_3(C_6H_5)(COOEt)_2$, and $C_6H_3(C_6H_5)_2(COOEt)$. Yield: 47 mg. MS (CI, *m*/*z*, %): $C_6H_3(C_6H_5)_2(COOEt)$, exact mass, 302.13: 303 (M + 1, 3.7), 302 (M, 4.1); $C_6H_3(C_6H_5)(COOEt)_2$, exact mass, 298.12: 299 (M + 1, 100), 298 (M, 71.0); $C_6H_3(COOEt)_3$, exact mass, 294.11: 295 (M + 1, 51.8), 294 (M, 9.4).

3.8. Catalytic polymerization reactions

A typical procedure in preparative scale is described as follows. To a solution of Rh(COD)($Ph_2PCH_2CH_2NTs$) (17.8 mg, 0.030 mmol) in THF (1 mL) was added dropwise a solution of phenylacetylene (0.165 mL, 1.50 mmol) in THF (4 mL) at room temperature. After the mixture was stirred for 2 h, the resulting mixture was diluted with THF (5 mL), and then added to MeOH (150 mL) to give a yellow precipitate, which was collected by filtration and washed with acetone (10 mL × 3), dried under vacuum. Yield: 0.11 g, 71%.

A typical procedure in NMR tube experiment is described as follows. A solution of complex **4** (5.4 mg, 9.1 μmol) and phenylacetylene (0.025 mL, 0.23 mmol) in $CDCl_3$ (0.40 mL) in a NMR tube was allowed to stand at room temperature for 50 min. An in situ ^{1}H NMR spectrum shows that the phenylacetylene was almost completely consumed. The product was precipitated out by addition of diethyl ether (25 mL). The solid was washed with methanol (2 mL), ether (5 mL) and dried under vacuum to give an orange-yellow powder. Yield: 9.1 mg, 39%. Similar results were obtained when [Rh(NBD)($Ph_2PCH_2CH_2NTs$)] was used as the catalyst. The molecular weight and molecular weight distribution M_w/M_n are given in Table 4.

NMR data for poly(phenylacetylene): ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 5.85 (br s, 1H,=CH), 6.64 (br s, 2H, *o*-Ph), 6.95 (br, 3H, *m*, *p*-Ph). ^{13}C {^{1}H} NMR (75.5 MHz, $CDCl_3$, 298 K): δ 126.8 (s, *p*-Ph), 127.7 (s, *o*- or *m*-Ph), 127.9 (s, *o*- or *m*-Ph), 131.9 (s, =CH), 139.4 (s, *ipso*-Ph), 143.0 (s, =CPh). The NMR data match those reported in the literature [11 g]. NMR data for poly(*p*-tolylacetylene): ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.2 (br s, 3H, CH3), 5.84 (br s, 1H, =CH), 6.34–6.66 (br s, 2H, C_6H_4), 6.66–7.08 (br, 2H, C_6H_4). Further details on the reaction conditions and polymer properties are given in Table 4.

3.9. Crystallographic analysis

Single crystals of **4** were obtained by layering hexane on top of a solution of the complex in benzene. Single crystals of **8** were obtained by slow evaporation of a solution of this complex in CH_2Cl_2–diethylether (1:7). Selected yellow crystals of **4** and **8**, with crystal sizes of 0.20 × 0.15 × 0.10 mm^3

Table 4
Polymerization of ArC≡CH catalyzed by [Rh(COD)($Ph_2PCH_2CH_2NTs$)][a]

Entry	Ar/[M] (mol/L)	[Cat] (mmol/L)	Solvent	Time[b]	M_w[c]	M_w/M_n[c]	Yield (%)[d]
1	Ph/0.56	23	$CDCl_3$	50 min	17800	1.55	39
2	Ph/1.5	15	C_6H_6	2 h	28600[e]	2.88	41
3	Ph/1.5	15	THF	2 h	63200	2.85	74
4	Ph/1.5	15	CH_2Cl_2	2 h	33300	2.25	44
5	Ph/0.30	6	THF	2 h	48100	2.61	71
6	*p*-Tolyl/0.30	3	THF	2 h	27100[e]	6.33	78

[a] All reactions were carried out at room temperature. Entry 1 was carried out in an NMR tube with 0.40 mL of $CDCl_3$. The rest were carried in preparative scale with ca. 5 mL of solvent.
[b] The reaction time is not optimized.
[c] Determined by GPC based on polystyrene standards.
[d] Isolated yields.
[e] Some polymer is insoluble in THF. M_w is referred to the portion soluble in THF.

and $0.20 \times 0.20 \times 0.15$ mm^3, respectively, were mounted on a glass fibre and transferred into the cold stream of nitrogen. Data collections were performed on a Bruker Apex CCD Area Detector by using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 100(2) K. Multi-scan absorption corrections (SADABS) [23] were applied. All structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on F^2 using Bruker SHELXTL (Version 5.10) program package [24]. All non-hydrogen atoms were refined anisotropically. Further details on crystal data, data collection and refinements are summarized in Table 1 and selected bond distances and angles are given in Tables 2 and 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge.

4. Supplementary material

Crystallographic Data Center as Supplementary Publications Nos. CCDC-264868 (**4**) and CCDC-264869 (**8**). Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK, fax: +44 1223 336 033; or email: deposit@ccdc.cam.ac.uk.

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