An Attractive Route to Olefin Metathesis Catalysts: Facile Synthesis of a Ruthenium Alkylidene Complex Containing Labile Phosphane Donors

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Abstract: Reaction of $RuHCl(PPh_3)_3$ **4** with 3-chloro-3-methyl-1-butyne effects transformation into $RuCl_2(PPh_3)_2(=CHCH=CMe_2)$ **1c**. Starting **4** is available commercially, or via quantitative reaction of $RuCl_2(PPh_3)_3$ with one equivalent of alkali phenoxides or isopropoxides in refluxing benzene-2-propanol. Phosphane exchange between **1c** and PCy_3 or 1,3-$(CH_2PCy_2)_2C_6H_4$ is rapid at RT, affording $RuCl_2(PCy_3)_2(=CHCH=CMe_2)$ **1b** or the novel alkylidene complex $RuCl_2[1,3\text{-}(CH_2PCy_2)_2C_6H_4](=CHCH=CMe_2)$ **7**. Much slower exchange occurred on use of $RuCl_2(PCy_3)_2(=CHPh)$ (**1a**) as precursor. Complex **1c** is stable indefinitely (months) in the solid state at RT under N_2, but dimerizes slowly in solution to give $RuCl(PPh_3)_2(\mu\text{-}Cl)_3Ru(PPh_3)_2(=CHCH=CMe_2)$ **6a**. 2,7-Dimethyl-octa-2,4,6-triene, the formal product of carbene coupling, is observed by ^1H NMR. Dimerization does not compete with phosphane exchange. A side-product arising from use of excess 3-chloro-3-methyl-1-butyne in the synthesis of **1c** was identified as Ru(IV) carbyne complex $RuCl_3(PPh_3)_2(\equiv CCH=CMe_2)$ **5**, the structure of which was confirmed by X-ray crystallography.

Keywords: alkylidenes; carbynes; metathesis; phosphanes; ruthenium

Introduction

The advent of well-defined transition metal alkylidene complexes has transformed the olefin metathesis reaction into a powerful, versatile tool for controlled synthesis of C-C bonds.[1–3] Key catalysts include highly active molybdenum imido complexes containing biphenolate or binaphtholate ligands, the applications of which encompass tactic ring-opening metathesis polymerization (ROMP)[2] and asymmetric ring-closing metathesis (ARCM).[3] The increased robustness of Ru complexes of the type $RuCl_2LL'(=CHR)$ (**1a**, $L = L' = PCy_3$, $R = Ph$; **2**, $L = PCy_3$, $L' =$ IMes, 1,3-dimesitylimidazol-2-ylidene, $R = Ph$) has significantly expanded the scope of metathesis chemistry.[1a] Issues of selectivity, however, are only beginning to be explored in the Ru systems, few examples of which incorporate a chiral ligand set.[4–6] Other key initiatives include ligand elaboration to permit supported[7] or water-soluble[8] Ru catalysis. Desirable, therefore, is a readily accessible "universal Ru precursor" that enables a modular approach to ligand tuning. In the absence of such a starting material, **1a** itself is widely used as a precursor to Ru alkylidene derivatives with alternative ligand sets, including **2**. Syntheses based on **1a** now outnumber all other routes to novel Ru alkylidenes, despite the comparatively low lability of the electron-rich donor PCy_3, and the multistep syntheses required. Routes to **1a** or closely related vinylalkylidenes [$L = L' = PCy_3$; $R = CH=CMe_2$ (**1b**[9]), $R = CH=CPh_2$[10]] utilize as precursors $Ru(COD)(COT)$,[11] $[RuCl_2(COD)]_n$,[12] $RuH_2(H_2)_2(PCy_3)_2$,[13] $RuHCl(H_2)(PCy_3)_2$,[9] $RuCl_2(PPh_3)_3$,[10,14,15] and $RuCl_3$.[16] Drawbacks include difficulties in synthesis of the pure hydrocarbon[10,14] or Ru[11] reagents, compounded in some cases by poor solubility,[12] instability of the Ru precursor,[11,13] requirements for use of H_2 gas,[9,13,16] or hazards associated with the hydrocarbon reagent.[14] We now report a straightforward, high-yield route to $RuCl_2(PPh_3)_2(=CHCH=CMe_2)$ **1c**, in one or two steps (respectively) from the commercially available complexes $RuHCl(PPh_3)_3$ **4** or $RuCl_2(PPh_3)_3$ **3**. We also describe an attractive alternative synthesis of **4**. Complex **1c** functions as a versatile precursor to other ruthenium alkylidene complexes, undergoing ligand exchange reactions under much milder conditions than those required for PCy_3 systems.

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Results and Discussion

Complex Synthesis

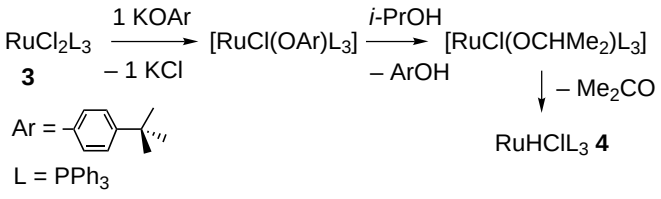
Phenoxide/Isopropoxide Route to $RuHCl(PPh_3)_3$

In the course of studies on Ru-phenoxide chemistry, we discovered that O-bound aryloxides undergo facile protonolysis by alcohols.[17] We have exploited this reactivity to develop an efficient, high-yield route to $RuHCl(PPh_3)_3$ **4**. Thus, addition of a 2-propanol solution of *p*-^{t}BuC$_6$H$_4$OK to **3** in benzene affords quantitative yields of purple **4** after 8 h at reflux. No other products are evident by ^{31}P NMR analysis under these conditions. Low solubility in this solvent mixture causes **4** to precipitate as it forms, precluding side-reactions. The proposed mechanism (Scheme 1) involves metathesis of aryloxide for chloride to form $RuCl(OAr)(PPh_3)_3$, which itself undergoes metathesis with 2-propanol to liberate the phenol (detected by ^{1}H NMR analysis). Facile β-elimination of acetone[18] from the isopropoxide intermediate thus formed yields the desired **4**. Exchange equilibria of phenols with less acidic alkoxide ligands such as methoxide have been utilized as an efficient route to phenoxo complexes.[19] The thermodynamically uphill metathesis of aryloxide by 2-propanol in the present systems is presumably driven by elimination of acetone. This route to **4**, utilizing a stable, solid phenoxide salt,[20] provides an attractive alternative to prior syntheses that required reaction of **3** with silanes, or with H_2 and base under high pressures or temperatures.[21]

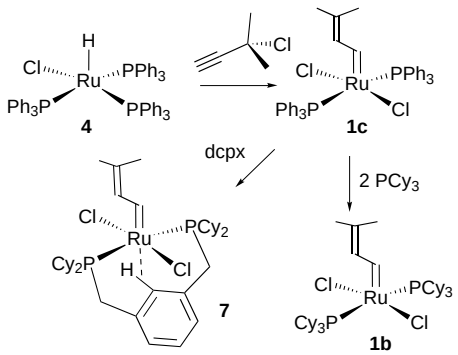
*Synthesis, Stability, and Phosphane Exchange of **1c***

We were intrigued by the potential utility of **4** as an entry point to a diverse array of alkylidene complexes, via reaction with 3-chloro-3-methyl-1-butyne[9] (affording **1c**), followed by exchange of the labile phosphane PPh_3 with suitable L-donor ligands (Scheme 2). Gram quantities of **4** are efficiently converted into **1c** within *ca.* 30 min at RT (22 °C) in CH_2Cl_2 solvent. ^{1}H NMR is diagnostic for this transformation: the upfield quartet for the hydride ligand of **4** (δ_H −17.8, $^2J_{HP}$ = 25.8 Hz) is replaced by a downfield quartet for H_α of the alkylidene (δ_H 18.20, $^3J_{HH} = {}^3J_{HP}$ = 9.4 Hz). The broad ^{31}P{^{1}H} NMR resonance at δ_P 57.5 for **4** simultaneously gives way to a sharp singlet for **1c** (δ_P 30.0). Subsequent phosphane exchange is conveniently carried out as a one-pot procedure from **4**. Thus, successive addition of 3-chloro-3-methyl-1-butyne and PCy_3 to **4** in CH_2Cl_2 effects quantitative conversion to known[9] $RuCl_2(PCy_3)_2$(=CHCH=CMe$_2$) **1b** within ∼40 min at RT. Stripping off the solvent, redissolving the residue in benzene, and filtering through Celite removes a small amount of insoluble black material. Concentration of the filtrate and addition of cold methanol affords purple **1b** in *ca.* 90% yield.

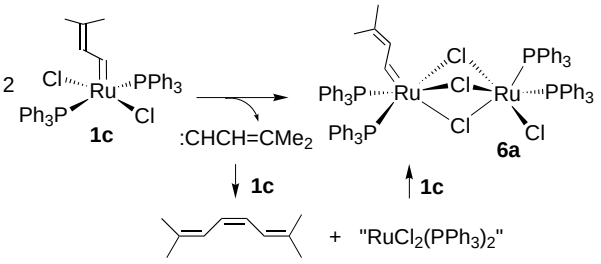
The observed black precipitate originates in small amounts (< 5%) of a carbyne contaminant present in **1c** (**5**, *vide infra*). Attempts to purify **1c** by isolation and reprecipitation prior to carrying out phosphane exchange offers no advantage, however. Instead, this procedure results in contamination of **1c** by dinuclear RuCl(PP)(μ-Cl)$_3$Ru(PP)(=CHCH=CMe$_2$) [**6a**, PP = $(PPh_3)_2$; Scheme 3], formed in solution via dimerization of **1c** and extrusion of alkylidene. (In the solid state, **1c** is stable for months under inert atmosphere at RT). We recently described dimerization of chelate complex $RuCl_2$(PP)(=CHCH=CMe$_2$) **1d** to yield **6b** [PP = dcypb, $Cy_2P(CH_2)_4PCy_2$; XRD and NMR evidence] and 2,7-dimethyl-octa-2,4,6-triene, and speculated that this chemistry might also be relevant to the monodentate Grubbs' systems.[22] Indeed, the ^{31}P{^{1}H} NMR pattern for **6a** in C_6D_6 [48.7 (br s, 1P), 43.9 (br s, 1P), 40.4 (br s, 2P)] closely resembles that observed for **6b** [δ_P 54.0 (br s, 1P), 46.1 (br s, 1P), 45.1 (br s, 1P), 42.9 (br s, 1P)]. *In situ* ^{1}H NMR analysis of **6a** reveals, in addition to the characteristic, complex olefinic AA'BB' pattern for the (*E*)- and (*Z*)-triene coproducts (Figure 1),[22] an alkylidene quartet at δ_H 16.9 ($^3J_{HH} = {}^3J_{HP}$ = 11.5 Hz), which HMQC experiments correlate with the ^{31}P signal at δ_P 40.4. The chemical shift and coupling constant correspond closely with the values for **6b** (δ_H 15.9; $^3J_{HH} = {}^3J_{HP}$ = 12.5 Hz). We note that **1c** dimerizes considerably more slowly than **1d**, presumably owing to the steric protection conferred by the *trans*-PPh_3 ligands within the former. Even after 10 days in solution in $CDCl_3$, *ca.*



Scheme 1. Proposed mechanism for phenoxide-mediated synthesis of **4**.



Scheme 2. Synthesis of alkylidene derivatives *via* **1c**.



Scheme 3. Solution dimerization of **1c** to **6a.**

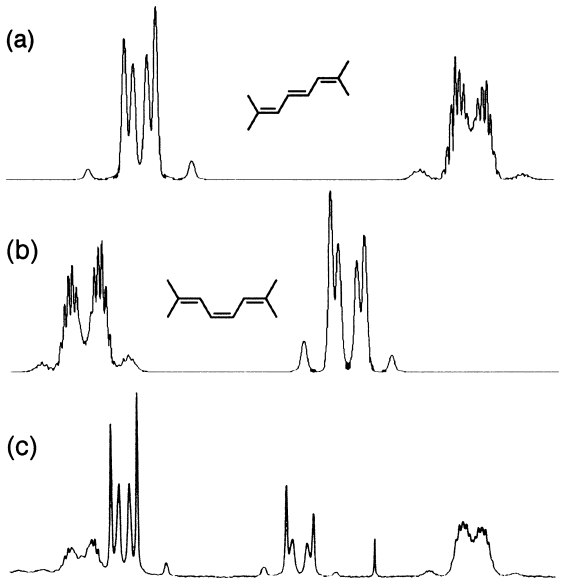


Figure 1. Olefinic AA'BB' signals for 2,7-dimethylocta-2,4,6-triene. (**a**) calcd., *E*-isomer; (**b**) calcd, *Z*-isomer; (**c**) experimentally observed.

15% **1c** remains. Dimerization proceeds even more slowly in benzene (54% after 11 days), but low solubility hampers quantification. Efforts to accelerate the reaction at reflux temperatures caused decomposition to additional, unidentified products, hampering isolation of **6a**.

Novel η^2-Pincer Alkylidene

Importantly, the slow solution decomposition of **1c** does not compete with phosphane exchange, as evidenced by the $\sim$90% isolated yield of **1b**. Reaction of **1c** with the bulky ligand 1,3-$(CH_2PCy_2)_2C_6H_4$ [bis(dicyclohexylphosphanyl)xylene; dcpx] in CH_2Cl_2 was likewise complete within 20 min at RT, affording $RuCl_2$[1,3-$(CH_2PCy_2)_2C_6H_4$](=CHCH=CMe_2) **7** (Scheme 2; isolated yields of **7** are limited to *ca.* 50% by high solubility). In comparison, use of **1a** as precursor resulted in only 50% conversion after 24 h. The higher lability of PPh_3, *vs.* PCy_3, has been invoked to rationalize the much higher metathesis activity of the PPh_3 derivative of $RuCl_2$ ($IMesH_2$)(PR_3)(CHPh) ($IMesH_2$ = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene).[23] The same feature renders the readily accessible complex **1c** an attractive alternative to **1a** or **1b** as a precursor to other alkylidene complexes.

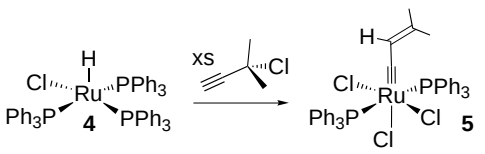
Complex **7** represents a virtually unexplored ligand architecture within Ru alkylidene complexes,[24] though such bulky diphosphanes have a rich catalytic and coordination chemistry with other late transition metals.[25] Coordination typically, though not invariably,[26] involves cyclometalation to give tridentate PCP-pincer complexes. While NMR and microanalytical data for **7** are consistent with complete displacement of PPh_3 by the dcpx ligand, C-H activation to form an η^3-pincer complex does not occur (though we do not exclude the possibility of a C-H agostic[26] interaction). The $^{31}P\{^1H\}$ NMR spectrum of **7** consists of a singlet (δ_P 19.4), consistent with a square pyramidal geometry containing basal, *trans*-disposed ^{31}P nuclei for the dcpx ligand. The triplet found for C_α (δ_C 301.3, $^2J_{PC}$ = 6.3 Hz) confirms the presence of only two ^{31}P nuclei on the metal center. The implied *cis*-disposition of the phosphanes with respect to the alkylidene is borne out by appearance of H_α as a doublet split only by H_β (δ_H 19.4, $^3J_{HH}$ = 11.6 Hz), indicating an H-C-Ru-P dihedral angle of 90° (as for **1b**[9]). Both pieces of evidence support apical siting of the alkylidene ligand. The ^1H NMR spectrum also reveals a singlet (δ_H 9.48, 1H) for the isolated dcpx proton, in addition to the expected triplet and doublet for the remaining aromatic protons. As with **1b**, synthesis of **7** is conveniently effected in a one-pot reaction from **4**. Importantly, we see no evidence for dimerization of **7** to give chloride-bridged species of the type noted for dcypb and PPh_3 systems above, presumably owing to the steric bulk of the dcpx ligand. The metathesis activity of **7** can be tuned from near zero to a potency in excess of that for $RuCl_2$(dcypb)(CHPh).[5b] Details of this chemistry will be reported separately.[27]

*Identification of Carbyne **5** in Reaction of **1c** with Propargyl Chloride*

Formation of small amounts ($<$5%) of carbyne **5** in the RT reaction of **4** with 3-chloro-3-methyl-1-butyne in CH_2Cl_2 was noted above. On carrying out the reaction on suspensions of **4** in THF, the proportion of **5** sometimes exceeded that of **1c**. Complex **5** was isolated in 75% yield on use of a fourfold excess of 3-chloro-3-methyl-1-butyne in THF, and identified as an Ru(IV) vinylcarbyne complex (Scheme 4) on the basis of detailed NMR and X-ray analysis. Key spectroscopic features include a carbyne signal in the $^{13}C\{^1H\}$ NMR spectrum (δ_C 304.5, $^2J_{PC}$ = 13.7 Hz), split into a triplet by the equivalent ^{31}P nuclei (δ_P 11.7, s). The singlet for C_β at 130.5 ppm, though obscured by overlap with the signal for the PPh_3 *para*-carbons, correlates with the olefinic

proton (δ_H 4.39) in ^1H-^{13}C HMQC experiments. The inequivalent methyl groups appear as independent singlets (δ_C 27.0, 26.2; δ_H 1.52, 1.19 ppm). A notable spectroscopic feature is the extreme downfield location of the quaternary olefinic carbon, in a region generally characteristic of the carbonyl functionality (δ_C 183.5). Unequivocal confirmation of our assignment comes from ^1H-^{13}C HMBC experiments, which correlate this signal with the olefinic proton, and with both sets of methyl protons. A similar value (δ_C 184.6) was cited for the olefinic carbon in $[RuCl(\equiv CCH{=}CPh_2)(\kappa^2\text{-P,O-}Cy_2PCH_2CH_2OCH_3)(\kappa\text{-}P\text{-}Cy_2PCH_2CH_2OCH_3)]^{2+}$.[28] The extreme deshielding of C_γ in these complexes may be due to contributions from a vinylidene resonance form that places a formal negative charge on this carbon. Consistent with this is the low stretching frequency for the ν(C=C) band in the IR spectrum of **7** (1571 cm^{-1}), as well as XRD data indicating a somewhat lengthened C=C bond [1.359(9) Å] and a short "single" bond between C_α and C_β in the subtended dimethylvinyl group [1.396(8) Å; *cf.* an average value of 1.491(9) Å for the C_γ-CH_3 bonds].

X-ray analysis also revealed the unexpected presence of a third chloride ligand (Figure 2). Formation of **5**, via net deprotonation and chlorination of **1c**, may indicate reaction between an Ru alkylidene species and a chloroalkyne molecule (the fate of which remains to be determined). We suspect that the actual culprit in this reaction may be a contaminant in the chloroalkyne reagent, as failure to distill the 3-chloro-3-methyl-1-butyne increased the proportion of **5** to 10% – 20%. Experiments directed at elucidating the origin and mechanism of this reaction are under way. The significance of this finding is underscored by the widespread interest in the propargyl chloride methodology as a route to alkylidene species independent of the toxic, mutagenic, and potentially explosive diazoalkanes.[29]



Scheme 4. Synthesis of vinylcarbyne **5.**

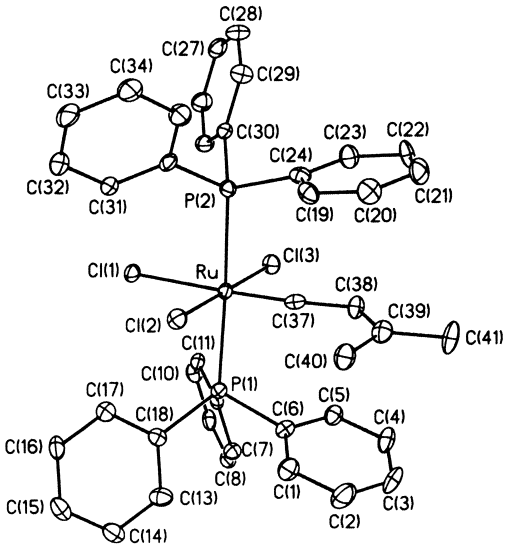


Figure 2. ORTEP diagram of **5**; hydrogen atoms and solvate molecules omitted. Thermal ellipsoids set at 30% probability level. Selected bond lengths [Å] and angles [°]: Ru-C(37) 1.696(6), Ru-P(1) 2.4552(16), Ru-P(2) 2.4447(16), Ru-Cl(1) 2.4940(16), Ru-Cl(2) 2.3971(16), Ru-Cl(3) 2.4173(16), C(37)-C(38) 1.396(8), C(38)-C(39) 1.359(9); P(1)-Ru-P(2) 177.46(6), Ru-C(37)-C(38) 170.7(5), C(37)-C(38)-C(39) 123.7(6).

Conclusions

Sequential reaction of $RuHCl(PPh_3)_3$ **4** with 3-chloro-3-methyl-1-butyne, followed by phosphane, provides an efficient, one-pot route to Ru alkylidene derivatives in high yields. The utility of this methodology was demonstrated by synthesis of PCy_3 derivative **1b**, as well as the novel 1,3-$(CH_2PCy_2)_2C_6H_4$ derivative **7**. Key to this chemistry is the lability of the PPh_3 ligands within intermediate **1c**, which permits rapid, efficient phosphane exchange at ambient temperatures. Dimerization of **1c** and extrusion of the alkylidene occurs over a timescale that does not compete with phosphane exchange. Bimolecular decomposition of **1** has long been recognized by the emergence of characteristic ^1H NMR signals for carbene "dimerization" products;[14] the foregoing provides the first clear indication of the fate of the Ru species. We speculate that a similar process may be involved in deactivation of the PCy_3 complexes, perhaps accompanied by loss of one phosphane ligand per Ru. The stoichiometry of the reaction affording **1c** is critical: in the presence of excess 3-chloro-3-methyl-1-butyne, **1c** undergoes unexpected deprotonation and chlorination, forming Ru(IV) carbyne **5**. Current efforts focus on identification of the origin of **5**, as well as development of hydrocarbon-soluble alternatives to **4**, which offer the possibility of stoichiometrically precise alkylidene installation and phosphane exchange, while obviating the requirement for non-chlorinated solvents.

Experimental Section

General Remarks

Reactions were carried out at RT (22 °C) in a N_2-filled drybox unless otherwise stated. 3-Chloro-3-methyl-1-butyne, *p-t*-BuC_6H_4OH and KH were purchased from Aldrich and used as received. $RuCl_2(PPh_3)_3$ **3** was prepared by the literature method,[30] phenoxides and alkoxides via reaction of KH with the appropriate phenol or alcohol. Dcpx [prepared as for 1,3-

$(CH_2P^tBu_2)_2C_6H_4$][26] was received as a gift from Prof. D. Gusev (Wilfrid Laurier University, Waterloo, ON). NMR spectra were recorded on a Bruker Avance-300 spectrometer (121.4 MHz for ^{31}P, 75.4 MHz for ^{13}C, 300 MHz for ^{1}H), IR spectra on a Bomem MB100 IR spectrometer. Microanalyses were carried out by Guelph Chemical Laboratories Ltd., Guelph, ON. Calculated spectra for (*E*)- and (*Z*)-2,7-dimethylocta-2,4,6-triene were obtained using the ACD/HNMR software package.

$RuHCl(PPh_3)_3$ 4

Method (a) *via* phenoxide salt: A solution of **3** (1.007 g, 1.05 mmol) in 40 mL C_6H_6 was treated with potassium *p*-*t*-butylphenoxide (0.198 g, 1.12 mmol) in 10 mL 2-propanol. The resulting solution was refluxed on a Schlenk line under N_2 for 8 h, resulting in formation of a purple suspension. The solvent was reduced in volume to $\sim$2 mL, and 10 mL hexane added, following which purple **4** was filtered off, washed with hexanes (4×5 mL) and methanol (4×3 mL) and dried under vacuum; yield: 0.940 g (97%). NMR data agree with values reported; see text.[31]

Method (b) *via* isopropoxide salt: A solution of potassium isopropoxide (1.15 mmol) in 8 mL dry 2-propanol was added to **3** (1.10 g, 1.15 mmol) in 45 mL benzene. Reaction and work-up as in (a) gave **4**; yield: 1.05 g (99%).

$RuCl_2(PPh_3)_2(=CHCH=CMe_2)$ 1c

Addition of freshly distilled 3-chloro-3-methyl-1-butyne (148 μL, 1.32 mmol) to a purple solution of **4** (1.11 g, 1.2 mmol) in 10 mL CH_2Cl_2 caused an immediate color change to brown. The solution was stirred for 30 min, then concentrated to $\sim$1 mL. Addition of 10 mL hexanes precipitated a brown solid, which was filtered off, washed with cold (−35 °C) hexanes (5×3 mL) and dried under vacuum; yield: 0.803 g (88%). A minor coproduct (< 5% of total integrated ^{31}P NMR intensity) was identified as carbyne complex **5** (*vide infra*). Reprecipitation from CH_2Cl_2/hexanes gave 0.762 g **1c** (83% yield), contaminated, however, with trace **6a**. ^{1}H NMR of **1c** ($CDCl_3$): δ = 18.20 (q, Ru=C*H*, 1H, $^3J_{HH} = {}^3J_{HP} = 9.4$ Hz), 6.85 – 7.65 (m, Ar + CHC*H*, 31H), 1.23 (s, CH_3, 3H), 0.96 (s, CH_3, 3H); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 30.0 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 291.4 (t, Ru=*C*, $^2J_{CP} = 10$ Hz), 152.1 (t, CH*C*H, $^3J_{CP} = 11$ Hz), 134.9 (t, Ar, $J_{CP} = 5.7$ Hz), 132.1 (t, Ph, $J_{CP} = 20$ Hz), 130.4 (s, Ph), 128.5 (t, Ph, $J_{CP} = 4.7$ Hz), 27.3 (s, *C*H_3), 20.9 (s, *C*H_3). IR (Nujol, cm^{-1}): ν(C=C) = 1568 (m); anal. calcd. for $C_{41}H_{38}Cl_2P_2Ru$: C 64.40, H 5.01%; found: C 63.85, H 5.36%; the discrepancy arises from the presence of trace **6a**.

One-Pot Synthesis of $RuCl_2(PCy_3)_2(=CHCH=CMe_2)$ 1b

3-Chloro-3-methyl-1-butyne (12.2 μL, 0.108 mmol) was added to a stirred solution of **4** (100 mg, 0.108 mmol) in 5 mL CH_2Cl_2 at RT. After 30 min, solid PCy_3 (60.6 mg, 0.216 mmol) was added, causing a color change to purple. After 10 min, the solvent was removed under vacuum, and the residue redissolved in benzene and filtered through Celite to remove small amounts of a black precipitate. The filtrate was concentrated, and 4 mL cold MeOH (−35 °C) added to precipitate the product as a purple solid, which was filtered off and washed with cold MeOH (3×2 mL). Yield after reprecipitation (C_6H_6 – MeOH) and drying under vacuum: 76 mg (88%). NMR parameters agree with the values reported[9] (see text).

$RuCl_3(PPh_3)_2(\equiv CCH=CMe_2)$ 5

Method (a): Addition of 3-chloro-3-methyl-1-butyne (122 μL, 1.08 mmol) to a stirred purple solution of **4** (250 mg, 0.27 mmol) in 5 mL THF caused an immediate color change to brown. After 72 h, orange solids precipitated, and no further **4** was evident by NMR analysis. The solution was diluted with hexanes (5 mL), and orange **5** filtered off, washed with hexanes (5×2 mL) and dried under vacuum. The limited solubility of **5** precluded reprecipitation; yield: 0.161 g (75%). ^{1}H NMR (CD_2Cl_2): δ = 8.02 (m, Ph, 12H), 7.35 (m, Ph, 18 H), 4.39 (s, C*H*, 1H), 1.52 (s, CH_3, 3H), 1.19 (s, CH_3, 3H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 11.7 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 304.5 (t, Ru ≡ *C*, $^2J_{CP} = 13.7$ Hz), 183.5 (s, Ru ≡ CCH=*C*), 135.3 (t, Ph, $J_{CP} = 4.9$ Hz), 132.1 (t, Ph, $J_{CP} = 23.6$ Hz), 130.5 (overlapping s, Ru ≡ C*C*H, Ph), 128.0 (t, Ph, $J_{CP} = 4.8$ Hz), 27.0 (s, *C*H_3), 26.2 (s, *C*H_3); IR (Nujol, cm^{-1}): ν(C=C) = 1571 (m); anal. calcd. for $C_{41}H_{37}Cl_3P_2Ru$: C 61.62, H 4.67%; found: C 61.20, H, 5.11%. X-ray quality crystals were obtained by slow evaporation of a THF solution.

Method (b): In CH_2Cl_2, the reaction is complete within 24 h, but competing dimerization results in coproduction of 30% of **6a**.

$RuCl(PPh_3)_2(\mu\text{-}Cl)_3Ru(PPh_3)_2(=CHCH=CMe_2)$ 6a

A suspension of **1c** (20 mg, 0.26 μmol) in 0.75 mL C_6D_6 underwent 54% conversion to **6a** over 11 d at RT. ^{1}H NMR (C_6D_6): δ = 15.86 (q, $^3J_{HH} = {}^3J_{HP} = 12.5$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 48.69 (br s, 1P), 43.89 (br s, 1P), 40.41 (br s, 2P).

$RuCl_2(\eta^2\text{-dcpx})(=CHCH=CMe_2)$ 7

Method (a): A solution of dcpx (66 mg, 0.13 mmol) in 1 mL CH_2Cl_2 was added dropwise to a stirred, brown solution of **1c** (100 mg, 0.13 mmol) in 7 mL CH_2Cl_2. After 20 min, the green solution was reduced to dryness and washed with cold (−35 °C) Et_2O and hexanes to afford pink **7**; yield: 42 mg (43%); the low yield is largely due to the partial solubility of **7**. ^{1}H NMR ($CDCl_3$): δ = 19.4 (d, Ru=C*H*, $^3J_{HH} = 11.6$ Hz, 1H), 9.48 (s, Ar, 1H), 8.13 (d, Ru=CHC*H*, $^3J_{HH} = 11.6$ Hz, 1H), 7.42 (t, Ar, $^3J_{HH} = 7.6$ Hz, 1H), 6.84 (d, Ar, $^3J_{HH} = 5.7$ Hz, 2H), 3.50 (br m, ArC*H*HP, 2H), 3.11 (br d, ArCH*H*P, $^2J_{HH} = 14.3$ Hz, 2H), 1.30 (s, CH_3, 6H), 0.9 – 2.6 (br, Cy, 44H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 19.5 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 301.3 (t, $^2J_{PC} = 6.3$ Hz, Ru=*C*); anal. calcd. for $C_{37}H_{60}Cl_2P_2Ru$: C 60.15, H 8.19%; found: C 59.79, H 7.96%.

Method (b), one-pot reaction from 4: The reaction was carried out as for **1b** above, and worked up as in (a), to afford **7** in 50% isolated yield.

Method (c): Reaction as above using **1a** as precursor showed only 50% conversion (^{31}P NMR) after 24 h.

X-Ray Crystallographic Study of 5

Molecular formula $C_{49}H_{53}Cl_3O_2P_2Ru$, $M = 943.27$, monoclinic, $P2(1)/c$, $a = 12.9747(11)$ Å, $b = 19.1933(17)$ Å, $c = 18.0307(16)$ Å, $\alpha = 90°$, $\beta = 92.711(2)°$, $\gamma = 90°$, $Z = 4$, $d = 1.397$ mg/m^3, $V = 4485.1(7)$ Å^3, absorption coefficient = 0.638 mm^{-1}, $T = 203(2)$ K, wavelength = 0.71073 Å, F(000) = 1952, Θ range = 1.57 to 20.81°, reflections collected/unique = 34618/4605 [R(int) = 0.1037], completeness to $\theta = 20.81$ 98.1%, crystal size = $0.13 \times 0.10 \times 0.04$ mm, limiting indices: $-12 \le h \le 12$, $0 \le k \le 19$, $0 \le l \le 18$, absorption correction: semi-empirical from equivalents, max. and min. transmission = 1.000000 and 0.781450, refinement method: full-matrix least-squares on F^2, data/restraints/parameters: 4605/0/442, Goodness-of-fit on $F^2 = 1.054$, $R = 0.0452$, $R_w = 0.0665$, $(R = \sum |(F_o - F_c)| / \sum |F_o|$; $R_w = [\sum[w(F_o^2 - F_c^2)^2] / \sum (wF_o^2)^2]^{1/2})$.

Details of Structural Analysis and Refinement

A suitable crystal was selected, mounted on a thin glass fiber using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in φ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.[32] Systematic absences in the diffraction data were uniquely consistent with the reported space group. The structure was solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2. Phenyl groups were treated as idealized, rigid, flat hexagons. Two molecules of THF were located cocrystallized in the asymmetric unit. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHEXTL 5.10 program library.[33] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-178713. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) + 44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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