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NAPHTHOQUINODIMETHANE COMPLEXES OF RUTHENIUM(0)*

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Abstract—Reactions of $[RuCl_2L_4]$ (L = PMe_3, PMe_2Ph or $PMePh_2$) with 2-lithiomethyl-1-methylnaphthalene or 2-lithiomethyl-3-methylnaphthalene lead to $[Ru(CH_2C_{10}H_6CH_2)L_3]$ which contain coordinated 1,2- or 2,3-naphthoquinodimethane moieties. Spectroscopic studies confirm these formulations and suggest significant localization of the double bonds, at least for the 1,2-naphthoquinodimethane fragment. For L = PMe_3 and 2-lithiomethyl-1-methylnaphthalene formation of the 1,2-naphthoquinodimethane complex is accompanied by the formation of $[Ru(CH_2C_{10}H_6CH_2)(PMe_3)_4]$ in which the organic moiety acts as a dialkyl, two-electron donor. Surprisingly for L = PMe_2Ph and 2-lithiomethyl-3-methylnaphthalene, the naphthoquinodimethane is not formed but the major product, although not isolated in a pure state, appears to be $[Ru(CH_2C_6H_{10}CH_3)Cl(PMe_2Ph)_3]$ in which the organic group is coordinated in an η^3 (allyl) mode. Plausible mechanisms, which account for the various products formed in these reactions are presented.

The stabilization of otherwise unstable organic compounds by coordination to transition elements is an area of particular interest, especially if the organic moiety can be released and undergo subsequent reactions. Perhaps the most spectacular early success in this area was the stabilization of cyclobutadiene by bonding to iron(0) and its subsequent release by oxidation.[1,2] More recently, a number of reports has appeared on the stabilization by coordination of *o*-quinodimethane,[3–9] which, although not stable itself, is an important intermediate in a range of organic synthetic reactions.[10] We[11] and others[12] have also reported that *o*-quinodimethane can be released from ruthenium or cobalt complexes by oxidation or ligand displacement and trapped by e.g. MeOOCC≡CCOOMe.

Most of the reported syntheses of *o*-quinodimethane complexes involve deprotonation[4,6] (or oxidation)[9] of hexamethylbenzene metal complexes, or reactions of *o*-bis(bromomethyl)benzene[3,5] or *o*-bis(chloromethyl)benzene derivatives.[8] Since these types of precursor are not always readily available for more complex aromatic systems, complexes of more elaborate analogues of *o*-quinodimethane have not been prepared.

In contrast we have reported that *o*-quinodimethane complexes of ruthenium[7] can be obtained directly from *o*-xylene by deprotonation with BuLi·TMED (TMED = 1,2-bis(dimethylamino)ethane) and reaction of the resulting lithium salt with, for example $[RuCl_2(PMe_3)_4]$. Since *o*-dimethylaromatic compounds are often readily available this reaction should be of more general applicability. Octamethylnaphthalene complexes of ruthenium(II) have been described,[13] but despite the fact that they have been reduced, deprotonation does not appear to have been attempted.

We now report the preparation of a series of 2,3-naphthoquinodimethane (**1**), and 1,2-naphthoquinodimethane (**2**) complexes prepared from 2,3-dimethylnaphthalene and 1,2-dimethylnaphthalene, respectively. A preliminary account of some of these results has appeared.[14]

RESULTS

Preparation of o-naphthoquinodimethane complexes of ruthenium

Reactions of a large excess of 2-lithiomethyl-3-methylnaphthalene·TMED with $[RuCl_2L_4]$ or of a large excess of 2-lithiomethyl-1-methylnaphthalene·TMED‡ with $[RuCl_2L_4]$ (L = PPh_2Me,

* Dedicated to Sir Geoffrey Wilkinson, on the occasion of his retirement from Imperial College, London.

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‡ It has been suggested[15] that this is the product obtained from the reaction of 1,2-dimethylnaphthalene with BuLi·TMED.

PMe_2Ph, or PMe_3) in diethyl ether leads to orange solutions for the 1,2-dimethylnaphthalene reactions and red solutions for the 2,3-dimethylnaphthalene reactions, from which compounds analysing as $[Ru(CH_2C_6H_{10}CH_2)L_3]$ may be isolated in reasonable yield.

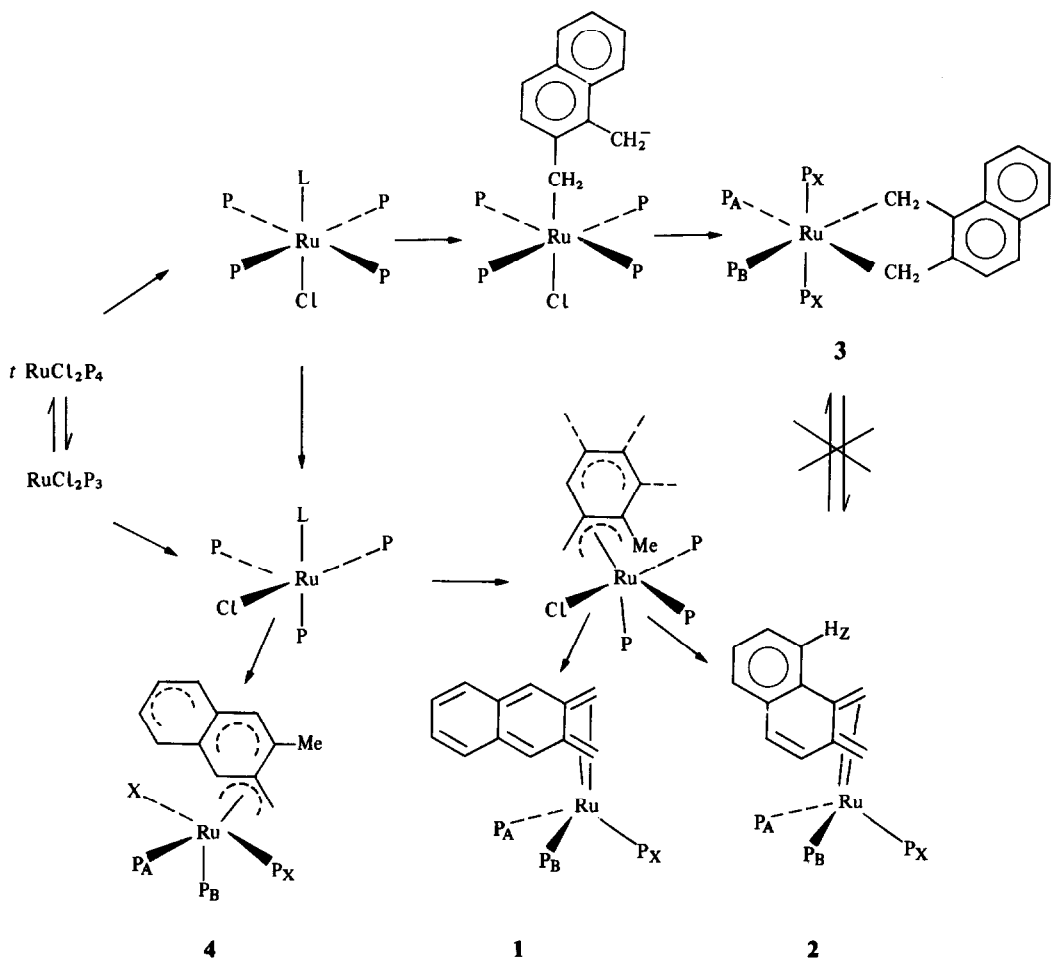
Although the major product isolated from the reaction of $[RuCl_2(PMe_3)_4]$ with 2-lithiomethyl-1-methylnaphthalene is the expected 1,2-naphthoquinodimethane complex, a second product, which analyses as $[Ru(CH_2C_{10}H_6CH_2)(PMe_3)_4]$ is also produced.

Somewhat surprisingly, the expected naphthoquinodimethane complex is not obtained from reaction of $[RuCl_2(PMe_2Ph)_4]$ with 2-lithiomethyl-3-methylnaphthalene but instead the major product appears, from spectroscopic studies (see below), to contain an intact $(CH_2C_{10}H_6CH_3)$ group bound in an η^3-allyl fashion.

We have attempted to interconvert $[Ru(CH_2C_{10}H_6CH_2)(PMe_3)_n]$ ($n = 3$ or 4) by refluxing the former with excess PMe_3 or by treating the latter with S_8 (a well known phosphine scavanger), photolysis or by extensive reflux in the absence of added phosphine, but in none of the cases is the interconversion achieved.

Spectroscopic properties

The ^1H and ^{31}P NMR spectra (Tables 1 and 2) of the 2,3-naphthoquinodimethane complexes are very similar to those of their *o*-quinodimethane analogues[7] with doublets of doublets being observed near δ 0 and 2 for the *endo* and *exo* methylene protons, respectively, pseudo doublets with some intensity between the lines arising from the $A_nXX'A'_n$ spin system of the methyl groups of the two symmetry related phosphines, and a doublet from the methyl group(s) of the unique phosphine. For $[Ru(CH_2C_{10}H_6CH_2)(PMe_3)_3]$, the resonances from the aromatic protons confirm that a plane of symmetry runs through the naphthalene ring. As for the related *o*-quinodimethane complexes,[7] J_{PP} in the ^{31}P NMR spectrum is small (< 11 Hz) con-



Scheme 1. Proposed mechanism for formation of compounds with structures **1–4**, L = $(CH_2C_{10}H_6CH_3)^-$.

Table 1. High field ^1H NMR data for new ruthenium complexes[a]

Complex	P_AMe $\delta(J_{PH})$	P_BMe $\delta(J_{PH})$	P_XMe $\delta(J_{PH})$	CH_{exo} $\delta(J_{PH})$	CH_{endo} $\delta(J_{PH})$	$J_{H_{exo}H_{endo}}$
$[Ru(2,3\text{-}CH_2C_{10}H_6CH_2)(PMePh_2)_3]$[b]	1.5 pd(4.1)[c]		2.2 d(7.8)	1.7 dd(5.5)	0.7 dd(4.5)	4.5
$[Ru(2,3\text{-}CH_2C_{10}H_6CH_2)(PMe_3)_3]$[d]	0.9 pd(6)[c]		1.4 d(8)	2.3 dd(8)	0.5 dd(5)	6
$[Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMePh_2)_3]$[e]	0.9 d(6)	1.35 d(6)	1.55 d(6)	2.55 m 2.0 m	0.4 bm[2H]	
$[Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMe_2Ph)_3]$	0.94 d(6) 0.99 d(6)	1.03 d(6) 1.16 d(6)	1.75 d(7)[6H]	2.35 bm[2H]	−0.4 bm[2H]	
$[Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMe_3)_3]$	0.7 d(6)	1.0 d(6)	1.5 d(8)	2.7 m 2.0 m	−0.2 bm[2H]	
$[Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMe_3)_4]$	1.4 d(5)	1.3 d(5)	0.9 pt(5)[c]	1.9 dd(5,11)[f]	2.45 ddt(4,9.5,9.5)[f]	

[a] Chemical shifts (δ) in ppm to high frequency of $SiMe_4$, coupling constants in Hz; measured in C_6D_6 at 298 K using C_6D_5H (δ 7.3) as internal reference; s = singlet, d = doublet, t = triplet, m = multiplet, p = pseudo (see text); for assignments, see Scheme 1.

[b] Measured in CH_2Cl_2 at 298 K using $CHDCl_2$ (δ 5.3) as internal standard.

[c] $J_{PH}+J_{PH'}$.

[d] Phenyl resonances, 7.8s (2H); 7.5 (AA'BB') (4H).

[e] Me assignments complicated by impurities.

[f] The two hydrogen atoms of each methylene group are equivalent.

Table 2. ^{31}P NMR data for new ruthenium complexes[a]

Complex	δP_A	δP_B	δP_X	$J(P_AP_X)$	$J(P_BP_X)$	$J(P_AP_B)$
$[Ru(2,3\text{-}CH_2C_{10}H_6CH_2)(PMePh_2)_3]$	19.5 d		41.4 t	4.0		
$[Ru(2,3\text{-}CH_2C_{10}H_6CH_2)(PMe_3)_3]$	0.16 d		28.5 t	10.7		
$[Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMePh_2)_3]$	15.6 d	20.3 d	30.2 s	0	0	24.2
$[Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMe_2Ph)_3]$	2.7 dd	4.1 dd	20.1 t	3.5	3.9	29.6
$[Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMe_3)_3]$	−9.8 dd	−6.3 dd	8.0 t	8.0	7.7	32.3
$[Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMe_3)_4]$	−20.7 dt	−14.8 dt	−6.15 t	26.5	25.1	13.8
$[Ru(CH_2C_6H_{10}CH_3)X(PMe_2Ph)_3]$	11.5 d	10.8 d	6.1 t	12.3	13.2	0

[a] Chemical shifts in ppm to high frequency of external 85% H_3PO_4, coupling contents in Hz; measured in C_6D_6 at 298 K; for assignments, see Scheme 1.

firming that the P—Ru—P angle is close to 100°. The rather larger value observed for the PMe_3 complex than for others containing bulkier phosphines may suggest a slightly smaller angle on account of reduced steric interaction. These compounds have structure **1**. For the 1,2-naphthoquinodimethane complexes, the lack of a plane of symmetry in the molecules means that more complex spectra are observed with separate doublets from the methyl groups on each phosphine and separate resonances showing coupling to several nuclei from the methylene hydrogen atoms. For L = PMe_2Ph, six doublet resonances are observed from the methyl groups since each pair is diastereotopic (no plane of symmetry runs through any of the phosphorus atoms).

In the ^{31}P spectra, separate resonances are observed for each phosphorus atom and the coupling constants are all small as expected for structure **2**.

The spectra of $[Ru(CH_2C_{10}H_6CH_2)(PMe_3)_4]$ show that it has structure **3**. Most indicative is the ^{31}P NMR spectrum which shows three resonances from the three distinct types of phosphorus atom, all with the couplings expected for *cis* phosphorus atoms in an octahedral complex. Two methylene resonances are observed at δ 1.88 and 2.43, the same region as that observed for the methylene protons in *o*-xylylidene complexes of e.g. platinum.[16,17] The methyl groups of the mutually *trans* phosphines resonate as a pseudotriplet ($A_9XX'A'_9$ with large J_{XX}), whilst doublets are observed from the other phosphine methyl groups.

Surprisingly, the product obtained from $[RuCl_2(PMe_2Ph)_4]$ and 2-lithiomethyl-3-methylnaphthalene · TMED is not the expected naphthoquinodimethane complex. Unfortunately, the complex has not been obtained in an analytically pure form, but resonances in the δ 3–6 region of the ^1H NMR spectrum are similar to those of the η^3 bound *o*-methylbenzyl ligand[18] in $[Rh(o\text{-}CH_2C_6H_4CH_3)(PPh_3)_2]$ although the multiplicities suggest more coupling to phosphorus. The ^{31}P NMR spectrum shows that there are three phosphine ligands in mutually *cis* positions. On this basis, we very tentatively assign the compound as **4** with X being either chloride or a σ bonded $o\text{-}CH_2C_{10}H_6CH_3$ ligand (it is not hydride). Microanalysis of an impure sample shows the presence of Cl so we favour Cl^- as the sixth ligand.

DISCUSSION

X-ray studies have shown[7] that there is significant bond localization in the *o*-quinodimethane group of $[Ru(CH_2C_6H_4CH_2)(PMe_2Ph)_3]$. The larger resonance energy of naphthalenes, which is presumably lost (especially for the 2,3-naphthoquinodimethane) if similar bond localization occurs in $\eta^2:\eta^2$ bonded *o*-naphthoquinodimethane complexes, makes it somewhat surprising that these complexes form so readily. However the spectroscopic data clearly show that this type of bonding does occur.

Although none of the complexes has given crystals of sufficient quality for X-ray structure determination so that a direct indication of the extent of bond localization is not possible, ^1H NMR studies do suggest that this localization does occur. Thus the phenyl region of the ^1H NMR spectrum of $[Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMe_3)_4]$, in which the organic moiety is bound as a simple dialkyl so that localization is not expected, is similar to that of the parent 1,2-dimethylnaphthalene. In contrast the phenyl region for $[Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMe_3)_3]$ in which $\eta^2:\eta^2$ bonding occurs, is quite different with one proton resonating at very low field (δ 8.35). The phenyl region of the spectrum of this compound is very similar to that of 1,2-naphthoquinone (low field resonance at δ 8.05),[19] in which the bonding is forced to be as in the localized bonding picture for **2**. The low field resonance then arises from proton Z. We therefore conclude that

significant bond localization does occur at least for the 1,2-naphthoquinodimethane complexes.

UV spectra

The UV spectra of $[Ru(2,3\text{-}CH_2C_{10}H_6CH_2)L_3]$ (L = $PMePh_2$ or PMe_3) show strong absorptions near 510 nm, which account for the dark red colour of the complexes. These absorptions are close to the position of the major absorption observed for matrix isolated 2,3-naphthoquinodimethane (541 nm),[20] suggesting again that significant delocalization occurs in the bound 2,3-naphthoquinodimethane complexes.

Mechanistic interpretation

The exact mechanism by which these complexes form is unclear, but since all attempts to interconvert $[Ru(CH_2C_{10}H_6CH_2)(PMe_3)_n]$ (n = 3 or 4) have failed, neither is on the reaction pathway to the other. It seems therefore that the loss of phosphine must occur at an early stage in the reaction but probably after alkylation of at least one Ru—Cl bond since we have shown[7] previously that loss of a phosphine from $[RuCl_2(PMe_3)_4]$ would allow alkylation by Grignard reagents, but that this reaction is not observed. For L = PMe_2Ph or $PMePh_2$, the phosphines are more labile, phosphine loss from the dihalides is known to be facile,[21] and alkylation by Grignard reagents is observed.[7]

The scheme affords a rational explanation for the formation of the various different observed products; which is supported by the following observations:

(i) We have shown that removal of a hydride from a methyl group α to a coordinated allyl moiety is facile in low valent ruthenium phosphine complexes.[22] In the case of the reaction involving PMe_2Ph and 2-lithiomethyl-3-methylnaphthalene, it may be that a marked preference for forming the allyl complex with the unsubstituted ring carbon atom (**4**) precludes the further deprotonation of the other methyl group.

(ii) $[RuCl_2(PMe_3)_4]$ has *trans* stereochemistry and attempts to isomerize it to *cis*, even under very forcing conditions, have not been successful.

It is probable, therefore that alkylation occurs *trans* to Cl^-. This will have two important consequences: firstly, the high *trans* effect of the alkyl ligand will labilize the remaining chloride and secondly the methyl group on the napthalene will become more acidic than that in 1,2-dimethylnaphthalene and hence be readily deprotonated by 2-lithiomethyl-1-methylnaphthalene·TMED. The formed anion clearly must attack the metal in a position *cis* to the bound methylene group and the lability of the Cl^- ligand will allow the formation of $[Ru(CH_2C_{10}H_6CH_2)(PMe_3)_4]$.

Unfortunately it is not clear why certain products are preferred for different combinations of L and dimethylnaphthalene.

EXPERIMENTAL

Microanalyses were carried out by St Andrews University laboratories. NMR spectra were recorded on Bruker WP-80, AM-300 and Varian CFT-20 spectrometers. All solvents were thoroughly dried by distillation from sodium benzophenone ketyl and degassed before use. The light petroleum had a boiling range of 40–60°C. All manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk-line and catheter tubing techniques. The compounds $[RuCl_2(PPh_3)_3]$,[23] $[RuCl_2(PMePh_2)_4]$,[24] $[RuCl_2(PMe_2Ph)_4]$[21] and $[RuCl_2(PMe_3)_4]$[25] were prepared by standard literature methods.

Preparation of lithium reagents

To a stirred solution of BuLi in hexane (6 cm^3, 9.6×10^{-3} mol, 1.6 M) cooled to 0°C was added TMED (3.0 cm^3, 19.8×10^{-3} mol). After 15 min the appropriate dimethylnaphthalene (1.56 g, 10×10^{-3} mol) in petroleum (40 cm^3) was added and the mixture stirred for a further 15 min before removing the ice bath and allowing the mixture to react for 24 h. The petroleum was removed by filtration and the lithium salt dissolved in diethyl ether (40 cm^3) ready for use. Assuming 100% conversion, the concentration of lithium reagent is 0.24 mol dm^{-3}.

Tris(methyldiphenylphosphine) (2-α,3-α′:η⁴-o-naphthoquinodimethane) ruthenium(0)

The complex $[RuCl_2(PPh_2Me)_4]$ (1.0 g, 1.028×10^{-3} mol) was stirred with a solution of 2-lithiomethyl-3-methyl naphthalene·TMED (40 cm^3, 0.24 mol dm^{-3}) in diethyl ether (40 cm^3). After 24 h, water (20 cm^3) was added to the red solution and after stirring for 30 min, the ether was decanted, dried over anhydrous sodium sulphate, and the ether removed *in vacuo*. Excess 2,3-dimethylnaphthalene and free $PMePh_2$ were removed by sublimation at 120°C onto a cold finger (−78°C). The resulting red gum was dissolved in the minimum amount of diethyl ether. After filtration and cooling to −30°C for several days, the product separated as red crystals, which were collected and dried *in vacuo*. Yield 0.35 (40%). Found: C, 70.7;

H, 7.0; P, 10.5. $C_{51}H_{49}P_3Ru$ requires: C, 71.6; H, 5.8; P, 10.9%.

The following complexes were similarly prepared, but with the work-up after the sublimation step as shown.

Tris(dimethylphenylphosphine) (1-α,2-α′:η^4-o-*naphthoquinodimethane*) *ruthenium*(0)

From $[RuCl_2(PMe_2Ph)_4]$ (0.75 g, 1.035×10^{-3} mol) and 2-lithiomethyl-1-methylnaphthalene·TMED (40 cm^3, 0.24 mol dm^{-3}). The orange gum was dissolved in diethyl ether (2 cm^3) and filtered into light petroleum (40 cm^3) precooled to −78°C. The yellow–orange precipitate was collected by filtration and dried *in vacuo*. However, ^{31}P NMR showed the product to contain *ca* 10% impurities. Yield 0.26 g (38%).

Tris(trimethylphosphine)(1-α,2-α′:η^4-o-*naphthoquinodimethane*) *ruthenium*(0)

From $[RuCl_2(PMe_3)_4]$ (0.55 g, 1.155×10^{-3} mol) and 2-lithiomethyl-1-methylnaphthalene·TMED (40 cm^3, 0.24 mol dm^{-3}) in diethyl ether (40 cm^3). The yellow gum was extracted with light petroleum (40 cm^3) to leave a yellow powder which was recrystallized from toluene and light petroleum, and identified as $[Ru(CH_2C_{10}H_6CH_2)(PMe_3)_4]$. Yield 0.07 g (11%). Found: C, 51.8; H, 8.2. $C_{24}H_{46}P_4Ru$ requires; C, 51.5; H, 8.3%.

The yellow petroleum solution was reduced in volume to 5 cm^3 and on cooling to −30°C gave yellow crystals which were collected and dried *in vacuo* and identified as $[Ru(CH_2C_{10}H_6CH_2)(PMe_3)_3]$. Yield 0.13 g (24%). Found: C, 52.3; H, 8.0. $C_{21}H_{37}P_3Ru$ requires: C, 52.5; H, 7.7%.

Tris(trimethylphosphine)(2-α,3-α′:η^4-o-*naphthoquinodimethane*) *ruthenium*(0)

From $[RuCl_2(PMe_3)_4]$ (0.55 g, 1.155×10^{-3} mol) and 2-lithiomethyl-3-methylnaphthalene·TMED (40 cm^3, 0.24 mol dm^{-3}). The red–brown solid was washed with light petroleum and dried *in vacuo*. Yield 0.22 g (40%). Found: C, 51.8; H, 7.5. $C_{21}H_{37}P_3Ru$ requires: C, 52.5; H, 7.7%.

Tris(methyldiphenylphosphine) (1-α,2-α′:η^4-o-*naphthoquinodimethane*) *ruthenium*(0)

From $[RuCl_2(PMePh_2)_4]$ (1.00 g, 1.028×10^{-3} mol) and 2-lithiomethyl-1-methylnaphthalene·TMED (40 cm^3, 0.24 mol dm^{-3}). The orange gum was dissolved in diethyl ether (1 cm^3) and syphoned into light petroleum (40 cm^3) precooled to −78°C. The resulting yellow solid which was collected and dried *in vacuo* was contaminated with $[H_2Ru(PPh_2Me)_4]$[26] (up to 20%) which could not be removed by further recrystallization. Yield 0.35 g.

Reaction of $[RuCl_2(PMe_2Ph)_4]$ *with* 2-CH_2-3-Me-$C_{10}H_6$

Reaction as above—from $[RuCl_2(PMe_2Ph)_4]$ (0.75 g, 1.035×10^{-3} mol) and 2-lithiomethyl-3-methylnaphthalene·TMED (40 cm^3, 0.24 mol dm^{-3}). The red–orange gum was extracted with hot petroleum (40 cm^3). After concentration a brown solid was formed. It could not be further purified but was tentatively assigned as $[Ru(\eta^3\text{-}CH_2C_{10}H_6Me)Cl(PMe_2Ph)_3]$ from its spectroscopic properties. ^1H NMR (C_6D_6) δ 6.5–8 m (Ph); 6.25 bt ($J = 7$ Hz) [1H]; 5.45 d ($J = 7.5$ Hz) [1H]; 4.0 q ($J = 9$ Hz) [1H]; 2.42 dd ($J = 6$, 6.5 Hz); 0.6–2.2 very complex series of doublets.

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