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REACTIONS OF TRANSITION METAL σ-ACETYLIDES

VIII *. PREPARATION AND PROPERTIES OF SOME ARYLDIAZO-VINYLIDENE COMPLEXES

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Summary

Fourteen aryldiazovinylidene complexes of ruthenium and osmium have been made by addition of aryldiazonium cations to the appropriate σ-acetylides. Their properties and spectra (including FAB-MS) are described, and reactions with MeOH, hydride and methoxide are reported. Addition to and protonation, alkylation, and cyclomanganation of the aryldiazo functions are also described.

Introduction

One of the characteristic reactions of transition metal σ-acetylide complexes, $M(C{\equiv}CR)(L)_n$, is their protonation or alkylation to give the related vinylidene complexes, $[M(C{=}CRR')(L)_n]^+$ (R′ = H or alkyl) [1]. This ready addition of electrophiles to the β-carbon of the acetylide fragment is consistent with theoretical findings that electron density in the HOMO is localised on this carbon [2]. It is surprising, therefore, that until our earlier reports [3,4] other electrophilic reagents have not been found to react in similar fashion with transition metal σ-acetylide complexes. Other types of reaction, in particular, cycloaddition of electron-deficient olefins [5], probably proceed via initial reaction at the β-carbon, but do not afford vinylidene complexes. This paper describes reactions of some ruthenium and osmium σ-acetylides with the electrophilic aryldiazonium cations to give the corresponding aryldiazovinylidene complexes; some of the results have been communicated briefly [3].

* For Part VII, see ref. 13.

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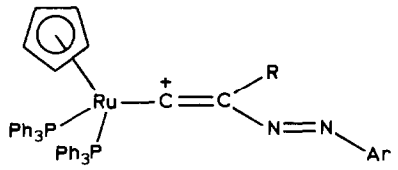
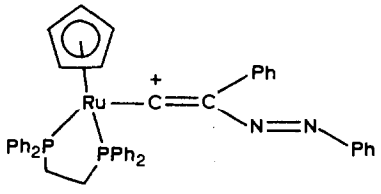
Results and discussion

Addition of $[ArN_2][PF_6]$ to an equimolar amount of $Ru(C{\equiv}CR)(L)_2(\eta\text{-}C_5H_5)$ in diethyl ether or tetrahydrofuran resulted in an immediate colour change from yellow to bright red. Suitable work-up procedures gave red crystalline solids which were



	R	Ar
1	Ph	Ph
2	Me	Ph
3	C_6F_5	Ph
6	Ph	$C_6H_3Me_2$-3,4
7	Me	$C_6H_3Me_2$-3,4
8	C_6F_5	$C_6H_3Me_2$-3,4

	R	Ar
9	Ph	$C_6H_4NO_2$-4
10	Me	$C_6H_4NO_2$-4
11	Ph	$C_6H_3Cl_2$-2,4
12	Me	$C_6H_3Cl_2$-2,4
13	Ph	C_6H_4OMe-4
14	Me	C_6H_4OMe-4



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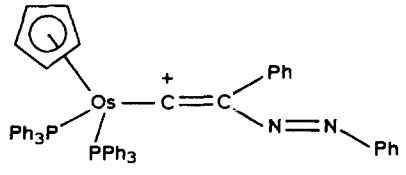

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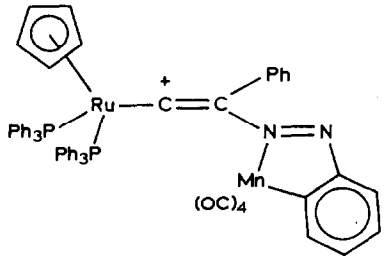

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identified in each case as the salts $[Ru(C{=}CRN{=}NAr)(L)_n(\eta\text{-}C_5H_5)][PF_6]$ by elemental microanalyses, from their spectral properties, and in one case, by a single-crystal X-ray diffraction study. Complexes **1–14** were obtained in this manner.

Their IR spectra contain medium intensity bands between 1550–1600 cm^{-1} assigned to ν(C=C) and ν(N=N) modes, and the usual strong broad absorption at ca. 840 cm^{-1} for the ν(PF) absorption from the PF_6^- anion. In the ^1H NMR spectra, the C_5H_5 resonances occur as singlets at δ ca. 5.3, and other resonances are characteristic of the various functional groups present in R, L or Ar. The ^{13}C NMR spectra contained C_5H_5 resonances at δ ca. 95, characteristic of cationic complexes; most informative were the resonances of the α- and the β-carbons of the vinylidene ligand, which were found at δ ca. 360 and 120 ppm, respectively. The former appeared as a triplet by coupling with the two ^{31}P nuclei, and its low-field position is typical for vinylidene complexes. These signals are relatively weak, however, and were not always located, even with the aid of paramagnetic reagents ($Cr(acac)_3$ or $Fe(acac)_3$) and delayed pulse techniques.

The formation of these complexes represents a facile synthesis of the C=C–N=N system and formation of a C–N bond. However, preliminary studies of the reactivity of these novel complexes indicate that the C–N bond is readily broken, regenerating the original metal acetylide complex. Thus, with PPh_3 or dppe, complex **1** afforded $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (50–80% recovery) and white organophosphorus compounds tentatively identified as $R_3P{=}NPh$.

Reagents which have been shown to react with $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ gave similar products with the aryldiazovinylidene complexes. Thus, after heating in refluxing aqueous tetrahydrofuran, complex **1** gave $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ in 70% yield. Similarly, a lower yield of $[Ru\{C(OMe)CH_2Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ was obtained in refluxing methanol. Displacement of the vinylidene ligand occurred under CO (45 atm, 100°C, 16 h); $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ was isolated in 37% yield, while a similar reaction with H_2, followed by treatment with a chlorinated solvent, afforded $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$. With iodomethane, the disubstituted vinylidene complex $[Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ was formed. In all of these cases, TLC examination of the solutions left after isolating the metal-containing complexes showed them to contain complex mixtures; we were not able to isolate and characterise any of these compounds.

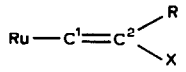
Reactions between **1** and $K[BH(CHMeEt)_3]$ (*K*-Selectride) or NaOMe afforded only $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$, recovered in very small amount (5–15%). Attempted protonation, (with $HPF_6 \cdot OEt_2$) gave only a partial hydrolysis product, the salt $[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][PO_2F_2]$, characterised on the basis of strong bands at 1590 (ν(C=C) + ν(N=N)), 1057 (ν(PO)) and 847 cm^{-1} (ν(PF)).

We were able to alkylate the diazo function in complex **1** with $[Me_3O]^+$. This slow reaction afforded yellow-brown $[Ru(C{=}CPhN{=}NMePh)(PPh_3)_2(\eta\text{-}C_5H_5)]^{2+}$, isolated as the mixed $PF_6^-/SbCl_6^-$ salt. Characterisation of this complex was aided by the N*Me* resonance found at δ 1.57 in the ^1H NMR spectrum.

A characteristic reaction of aryldiazo groups is their cyclometallation which occurs on reaction with many metal substrates. The reaction between **1** and $Mn(CH_2Ph)(CO)_5$ afforded a purple complex, characterised as the metallated complex **15**. The IR spectrum contained three ν(CO) absorptions at 2080, 1999 and 1959 cm^{-1}, confirming the presence of the $Mn(CO)_4$ group, while fast atom bombardment mass spectrum contained a parent ion and related fragment ions. X-ray quality crystals have not been obtained.

TABLE 1

STRUCTURAL PARAMETERS FOR RUTHENIUM-VINYLIDENE COMPLEXES



R	X	Bond distances (Å)		Bond angles (°)			Ref.
		Ru–C(1)	C(1)–C(2)	Ru–C(1)–C(2)	C(1)–C(2)–R	C(1)–C(2)–X	
Ph	C_7H_7	1.848(9)	1.32(1)	174.9(6)	121.1(6)	118.1(7)	[3]
Me	H	1.845(7)	1.313(10)	180(2)	125.1(6)	–	[10]
Me	Ph	1.863(10)	1.293(15)	172.8(11)	117.0(11)	125.1(12)	[11]
Ph	$N{=}NC_6H_3Me_2$	1.823(9)	1.34(1)	169.9(7)	121.4(8)	114.4(8)	[3]
C_6H_4Br-4	Br	1.85(1)	1.31(2)	169.4(14)	126.8(15)	116.8(13)	[4]

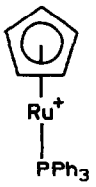
The molecular structure of $[Ru(C{=}CPhN{=}NC_6H_3Me_2\text{-}3,4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ has been reported previously [3], and confirms the presence of the aryldiazovinylidene ligand. Table 1 compares some structural parameters in a range of vinylidene complexes. The Ru–C(1) distance of 1.823(9) Å is one of the shortest such separations known, while the C(1)–C(2) distance of 1.34(1) and angles about the β-carbon (C(1)–C(2)–N(1) 114.4(8), C(1)–C(2)–C(Ph) 121.4(8), C(Ph)–C(2)–N(1) 124.2(7)°) indicate a normal C=C double bond and relatively little distortion from a trigonal sp^2-hybridised C(2). The Ru–C(1)–C(2) system is nearly linear (169.9(7)°). The aryldiazo group has the *trans* configuration usually found, with no significant differences in bond parameters from those found in *trans*-azobenzene, e.g. N(1)=N(2) 1.27(1), N(2)–C(Ar) 1.42(1) Å, N(1)–N(2)–C(Ar) 113.0(7)°.

Fast atom bombardment mass spectra

The technique of ionisation of substrates by fast atom bombardment (FAB) has extended the utility of mass spectrometry to the analysis of both high molecular weight and ionic materials. Its application to organometallic molecules was demonstrated in the first account [6], and a wide variety of studies have been described and reviewed [7]. FAB ionisation is admirably suited to complexes such as those described in this paper, and we have recorded the spectra of complexes **5**, **8**, **10** and **15**.

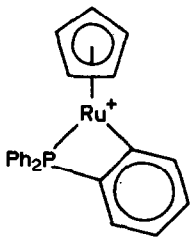
All spectra contain ions corresponding to the cation; the osmium complex has a matrix adduct ion at highest m/z value. Two major fragmentation routes for the molecular cation are loss of PPh_3 or of the aryldiazo fragment, which latter parallels the chemistry; in the case of **8**, loss of arylnitrene also occurs, while with **10**, loss of N_2 gives an ion at m/z 958. The base peaks are centred on m/z 427 ($[Ru(PPh_3)(\eta\text{-}C_5H_5) - nH]^+$) for the ruthenium complexes; for the osmium complex **10**, the analogous ion at m/z 518 is found, but is exceeded in intensity by the phosphido ion, $[Os(PPh_2)(C_5H_5)]^+$.

Comparisons with electron impact (EI) generated spectra cannot be direct, since these ionic complexes do not give EI spectra; however, spectra of related neutral complexes $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$ are generally characterised by weak molecular ions, ready loss of X and PPh_3, with base peaks centred on m/z 427. We have previously suggested that ions at m/z 427, 428 and 429 have the composition



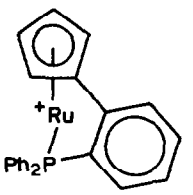
m/z 429

(A)



m/z 428

(B)



m/z 427

(C)

$[Ru(PPh_3)(C_5H_5) - nH]^+$ ($n = 2$, 1 and 0 respectively), with structures such as **A**, **B** and **C**; molecular complexes containing these structural fragments are known [8]. The FAB spectra contrast with EI spectra in having increased relative intensities of ions containing two PPh_3 ligands and in preserving the Ru–element bond in the fragment **X** (in this case the Ru–C bond to the vinylidene ligand).

The spectrum of the cyclometallated complex (**15**) has also been obtained. In this, the highest ion corresponds to the cation, which then loses five fragments of 28 m.u. (four CO + N_2). Subsequent fragmentation is similar to that found for complex (**5**), with loss of N_2, N_2Ph, PPh_3 and Ph fragments; an ion at *m/z* 719 corresponds to the carbonyl cation $[Ru(CO)(PPh_3)_2(C_5H_5)]^+$.

Experimental

General conditions. All reactions were run under nitrogen except those involving CO or H_2; no special precautions were taken to exclude air during work-up, since most complexes proved to be stable in air as solids, and for short times in solution. Solvents were dried and distilled (dme and thf from sodium diphenylketyl) before use. Pressure reactions were carried out in a small stainless steel laboratory autoclave (Carl Röth, Karlsruhe) of internal volume 100 ml, equipped with an internal glass liner.

Instruments. Perkin–Elmer 683 double-beam spectrometer, NaCl optics (IR); Bruker WP80 spectrometer (^1H NMR at 80 MHz, ^{13}C NMR at 20.1 MHz); GEC-Kratos MS3074 mass spectrometer (mass spectra at 70 eV ionising energy, 4 kV accelerating potential).

FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, current 1 mA. The ion accelerating potential was 8 kV. The matrix was 6/1 dithiothreitol/dithioerythritol or 3-nitrobenzyl alcohol (**15**). The complexes were made up as ca. 0.5 *M* solutions in acetone or dichloromethane; a drop was added to a drop of matrix and the mixture was applied to the FAB probe tip.

Starting materials. The ruthenium and osmium acetylide complexes were prepared by the literature methods [9], while the aryldiazonium salts were made by diazotisation of the appropriate substituted aniline with $NaNO_2/HBF_4$; $[PhN_2][PF_6]$ was obtained from Cationics Inc., Cleveland, Ohio, and vacuum dried prior to use.

Chromatography. In column chromatography Florisil or silica was used as adsorbent; preparative TLC was on 20 × 20 cm plates coated with Kieselgel 60 GF_{254} (Merck, Darmstadt).

Preparation of aryldiazovinylidene complexes

(a) [Ru(C=CPhN=NPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (1). A suspension of Ru(C≡CPh)(PPh$_3$)$_2$(η-C$_5$H$_5$) (200 mg, 0.253 mmol) in tetrahydrofuran (10 ml) was treated with an excess of a suspension of [PhN$_2$][PF$_6$] in diethyl ether. A red-orange solution formed immediately. After stirring the solution for 10 min, the solvent was removed in vacuo; a dichloromethane extract of the residue was filtered, and addition of methanol to the filtrate followed by slow evaporation afforded red crystals of [Ru(C=CPhN=NPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (**1**) (226 mg, 86%), m.p. 177–181°C (dec.) (Found: C, 63.1; H, 4.4; N, 2.7; $C_{55}H_{45}F_6N_2P_3Ru$ calc: C, 63.4; H, 4.4; N, 2.7%). Infrared (Nujol): ν(C=C) + ν(N=N) 1585m, ν(PF) 835s(br) cm^{-1}; other bands at 1437m, 1408w, 1308w, 1233w, 1195w, 1155w, 1090m, 1075w, 1020w, 999w, 973w, 930w, 922w, 898w, 875w, 777w, 745m, 713m, 649s cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 5.28 (s, 5H, C_5H_5), 7.26 (m, 40H, Ph). ^{13}C NMR: δ ($CDCl_3$) 96.45 (C_5H_5), 122.18 (RuC=*C*), 128.86–133.83 (Ph), 125.38, 153.49, 160.44 (N=NPh), 362.01 (t, *J*(CP) 15.8 Hz, RuC).

The following complexes were prepared similarly:

(b) [Ru(C=CMeN=NPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] · 0.5CH$_3$OH (2), from Ru(C≡CMe)(PPh$_3$)$_2$(η-C$_5$H$_5$) (200 mg, 0.274 mmol), as red-orange crystals (263 mg, 96%), m.p. 183–187°C (dec.) (Found: C, 60.0; H, 4.5; N, 2.8; $C_{50}H_{43}F_6N_2P_3Ru \cdot 0.5CH_4O$ calc: C, 60.9; H, 4.6; N, 2.8%). Infrared (Nujol): ν(C=C) + ν(N=N) 1608m; ν(PF) 835s(br) cm^{-1}; other bands at 1438w, 1300w, 1220w, 1175m, 1146w, 1090m, 1070w, 1038s, 1000w, 973w, 878w, 852s, 825s, 776w, 746m, 738w, 720w, 700m, 688m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 1.91 (s, 3H, Me), 3.48 (s, 1.5H, MeO), 5.35 (s, 5H, C_5H_5), 7.42 (m, 35H, Ph).

(c) [Ru{C=C(C$_6$F$_5$)N=NPh}(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] · CH$_3$OH (3), from Ru(C≡CC$_6$F$_5$)(PPh$_3$)$_2$(η-C$_5$H$_5$) (200 mg, 0.226 mmol), as orange crystals (130 mg, 49%), m.p. 145–147°C (dec.) (Found: C, 56.9; H, 3.7; N, 2.3; $C_{55}H_{40}F_{11}N_2P_3Ru \cdot CH_4O$ calc: C, 57.8; H, 3.8; N, 2.4%). Infrared (Nujol): ν(C=C) + ν(N=N) 1590m, ν(PF) 835s(br) cm^{-1}; other bands at 1514m, 1494m, 1440m, 1415w, 1308w, 1161w, 1151w, 1090m, 1080w, 1018w, 998w, 984w, 941w, 900w, 764m, 746m, 717w, 693s cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 3.47 (s, 3H, OMe), 5.49 (s, 5H, C_5H_5), 7.32 (m, 35H, Ph). ^{13}C NMR: δ ($CDCl_3$) 97.54 (C_5H_5), 122.49 (RuC=*C*), 128.90–133.20 (Ph). 44 mg (22%) Ru(C≡CC$_6$F$_5$)(PPh$_3$)$_2$(η-C$_5$H$_5$) was recovered.

(d) [Os(C=CPhN=NPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (5), from Os(C≡CPh)(PPh$_3$)$_2$(η-C$_5$H$_5$) (80 mg, 0.091 mmol), as orange crystals (96 mg, 93%), m.p. 202–205°C (dec.) (Found: C, 58.10; H, 4.04; N, 2.49; $C_{55}H_{45}F_6N_2OsP_3$ calc: C, 58.40; H, 4.01; N, 2.48%). Infrared (Nujol): ν(C=C) + ν(N=N) 1593s; ν(PF) 839s(br) cm^{-1}; other bands at 1445w, 1440m, 1418w, 1311w, 1242m, 1200w, 1158w, 1093m, 1072w, 1028w, 1024w, 1019w, 1001w, 937w, 922w, 907w, 779w, 752w, 748w, 718m, 699m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 5.43 (s, 5H, C_5H_5), 7.23 (m, 40H, Ph). ^{13}C NMR: δ ($CDCl_3$) 93.58 (C_5H_5), 122.20 (OsC=*C*), 128.39–134.93 (Ph), 124.30, 153.38, 158.99 (N=NPh).

(e) [Ru(C=CPhN=NPh)(dppe)(η-C$_5$H$_5$)][PF$_6$] (4) (by E. Poczman), from Ru(C$_2$Ph)(dppe)(η-C$_5$H$_5$) (200 mg, 0.30 mmol) and [PhN$_2$][PF$_6$] (310 mg, 1.24

mmol) in thf (20 ml), as an orange powder (from CH_2Cl_2/MeOH), m.p. 172–175°C (dec.) (Found: C, 57.62; H, 4.24; N, 2.99; $C_{45}H_{39}F_6N_2P_3Ru$ calc: C, 59.06; H, 4.29; N, 3.06%). Infrared (Nujol): ν(N=N) and ν(C=C) 1608s, 1577m; ν(PF) 840vs(br); other bands at 1445(sh), 1420(sh), 1400m, 1380m, 1310(sh), 1235m(br), 1100(sh), 1060m, 899m, 870m, 775m, 730m, 710m, 695m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 5.45 (s, 5H, C_5H_5), 7.57 (m, 30H, Ph).

(f) [Ru(C=CPhN=NC$_6$H$_3$Me$_2$-3,4)(PPh$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] (6) was prepared from $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.253 mmol) and [3,4-$Me_2C_6H_3N_2$][BF_4] (56 mg, 0.253 mmol) in dichloromethane (10 ml). The yellow solution became red immediately. After stirring for 5 min, the volume was reduced to 5 ml and the solution filtered into diethyl ether (100 ml), precipitating [Ru(C=CPhN=$NC_6H_3Me_2$-3,4)(PPh_3)$_2$(η-C_5H_5)][BF_4] as an orange powder (224 mg, 88%), m.p. 144–146°C (dec.). This was crystallised from a dichloromethane/methanol mixture as the 0.67 methanol solvate (Found: C, 66.4; H, 5.0; N, 2.7; $C_{57}H_{49}BF_4P_2Ru \cdot 0.67CH_4O$ calc: C, 66.3; H, 5.0; N, 2.7%). Infrared (Nujol): ν(C=C) + ν(N=N) 1588s, 1575m; ν(BF) 1060s(br) cm^{-1}; other bands at 1488w, 1472m, 1442s, 1434s, 1418w, 1315w, 1285w, 1241w, 1223m, 1190w, 1161w, 1150w, 999m, 889w, 856m, 839m, 826m, 798w, 752m, 747m, 720w, 695s, 673m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 2.14 (s, 3H, Me), 2.29 (s, 3H, Me), 3.48 (s, 2H, MeO), 5.32 (s, 5H, C_5H_5), 7.07–7.40 (m, 38H, Ph). ^{13}C NMR: δ ($CDCl_3$) 19.57 (Me), 96.06 (C_5H_5), 125.43 (RuC=*C*), 128.68–135.82 (Ph), 119.88, 123.02, 151.97, 160.14 (N=NC_6).

(g) [Ru(C=CMeN=NC$_6$H$_3$Me$_2$-3,4)(PPh$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] (7), from $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.274 mmol) and [3,4-$Me_2C_6H_3N_2$][BF_4] (60 mg, 0.274 mmol), as an orange powder (225 mg, 87%), m.p. 182–184°C (dec.) (Found: C, 65.6; H, 5.1; N, 2.9; $C_{52}H_{47}BF_4P_2Ru$ calc: C, 65.8; H, 5.0; N, 3.0%). Infrared (Nujol): ν(C=C) + ν(N=N) 1617s; ν(BF) 1042s(br) cm^{-1}; other bands at 1442m, 1372s, 1321w, 1312w, 1289w, 1281w, 1247w, 1208w, 1190w, 1172w, 1160w, 1098m, 1075m, 1062m, 1028m, 1001w, 888w, 853w, 839w, 825w, 762w, 747w, 727w, 702w, 698m, 668w cm^{-1}. ^1H NMR: δ ($CDCl_3$) 1.92 (s, 3H, C=CMe), 2.18 (s, 3H, Me), 2.31 (s, 3H, Me), 5.38 (s, 5H, C_5H_5), 7.27 (m, 33H, Ph). ^{13}C NMR: δ ($CDCl_3$) 7.02 (C=CMe), 19.47 (Me), 95.72 (C_5H_5), 128.57–138.30 (Ph), 119.58, 122.71, 151.69, 155.98 (N=NC_6).

(*h*) Following the method in (e) above, $Ru(C{\equiv}CC_6F_5)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.227 mmol) and [3,4-$Me_2C_6H_3N_2$][BF_4] (50 mg, 0.227 mmol) afforded a red-orange solution. The solvent was removed in vacuo and a dichloromethane extract of the residue was chromatographed (silica TLC plates; 1/1 acetone/light petroleum eluant), giving seven bands. The major band, red (R_f 0.60), was crystallised (dichloromethane/methanol), affording *[Ru(C=CC$_6$F$_5$N=NC$_6$H$_3$Me$_2$-3,4)(PPh$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] · MeOH (8)* (146 mg, 58%), m.p. 166–167°C (dec.) (Found: C, 61.47; H, 4.17; N, 2.47; $C_{57}H_{44}BF_9P_2Ru \cdot CH_4O$ calc: C, 61.44; H, 4.27; N, 2.47%). Infrared (Nujol): ν(C=C) + ν(N=N) 1597s; ν(BF) 1072s(br) cm^{-1}; other bands at 1517m, 1493s, 1482m, 1440m, 1435m, 1415m, 1310m, 1281w, 1268w, 1238w, 1189w, 1164m, 1090s, 985s, 939w, 882w, 859w, 850m, 838m, 824m, 747s, 718m, 695s cm^{-1}. ^1H NMR: δ ($CDCl_3$) 2.12 (s, 3H, Me), 2.28 (s, 3H, Me), 3.46 (s, 3H, OMe), 5.55 (s, 5H, C_5H_5), 7.25 (m, 33H, Ph). ^{13}C NMR: δ ($CDCl_3$) 19.47 (Me), 97.37 (C_5H_5), 128.57–139.66 (Ph), 120.06, 123.27, 151.53 (N=NC_6).

(i) [Ru(C=CPhN=NC$_6$H$_4$NO$_2$-4)(PPh$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] · 0.1CH$_3$OH (9), from

$Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.253 mmol) and $[4\text{-}O_2NC_6H_4N_2][BF_4]$ (60 mg, 0.253 mmol), and crystallised (dichloromethane/methanol) as maroon crystals (180 mg, 69%), m.p. 203–205°C (dec.) (Found: C, 63.81; H, 4.18; N, 3.79; $C_{55}H_{44}BF_4N_3O_2P_2Ru \cdot 0.1CH_4O$ calc: C, 64.13; H, 4.34; N, 4.07%). Infrared (Nujol): ν(C=C) + ν(N=N) 1605w, 1582m, 1565m; ν(NO) 1525m, 1338s; ν(BF) 1050s(br) cm^{-1}; other bands at 1438s, 1418w, 1295w, 1282w, 1261m, 1192w, 1181w, 1162w, 1154m, 1107w, 1090s, 1071s, 997m, 972s, 922w, 901w, 867m, 853w, 842w, 823w, 765w, 745m, 729m, 695s cm^{-1}. ^1H NMR: δ ($CDCl_3$) 3.47 (s, 0.3H, OMe), 5.39 (s, 5H, C_5H_5), 7.0–8.1 (m, 39H, Ph + C_6H_4). ^{13}C NMR: δ ($CDCl_3$) 96.99 (C_5H_5), 122.60, 124.37 (N=NC_6), 128.57–134.09 (Ph + C_6H_4).

(j) [Ru(C=CMeN=$NC_6H_4NO_2$-4)(PPh_3)$_2$(η-C_5H_5)][BF_4] · 0.5CH_2Cl_2 (10), from $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.274 mmol) and $[4\text{-}O_2NC_6H_4N_2][BF_4]$ (65 mg, 0.274 mmol), and crystallised (dichloromethane/methanol) as red crystals of the 0.5 dichloromethane solvate (233 mg, 85%), m.p. 218–220°C (dec.) (Found: C, 60.61; H, 4.29; N, 4.17; $C_{50}H_{42}BF_4N_3O_2P_2Ru \cdot 0.5CH_2Cl_2$ calc: C, 60.10; H, 4.29; N, 4.16%). Infrared (Nujol): ν(C=C) + ν(N=N) 1608w, 1597w, 1582m; ν(NO) 1517m, 1337s; ν(BF) 1037s(br) cm^{-1}; other bands at 1438m, 1418w, 1368s, 1357m, 1291w, 1230w, 1178m, 1148m, 1115w, 1105w, 1091m, 1078w, 1052m, 999w, 862w, 841w, 825w, 762w, 755w, 744m, 718w, 702w, 691m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 1.95 (s, 3H, Me), 5.32 (s, 1H, CH_2Cl_2), 5.47 (s, 5H, C_5H_5) 7.0–8.3 (m, 34H, Ph + C_6H_4).

(k) [Ru(C=CPhN=$NC_6H_3Cl_2$-2,4)(PPh_3)$_2$(η-C_5H_5)][BF_4] · 0.25Et_2O (11), from $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.253 mmol) and $[2,4\text{-}Cl_2C_6H_3N_2][BF_4]$ (66 mg, 0.253 mmol) as a red powder (234 mg, 85%), m.p. 191–194°C (dec.) (Found: C, 62.62; H, 4.26; N, 2.49; $C_{55}H_{43}BCl_2F_4N_2P_2Ru \cdot 0.25C_4H_{10}O$ calc: C, 62.79; H, 4.28; N, 2.62%). Infrared (Nujol): ν(C=C) + ν(N=N) 1582m, 1565m; ν(BF) 1071s(br) cm^{-1}; other bands at 1442w, 1437s, 1411w, 1402m, 1369s, 1353w, 1311w, 1279w, 1261w, 1243w, 1195w, 1182w, 1160w, 1091s, 1052s, 1035s, 995m, 919w, 900w, 855w, 838m, 822w, 791w, 758w, 746m, 695s, 683m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 1.18 (t, J(HH) 7.6 Hz, 1.5H, CH_3), 3.47 (q, J(HH) 7.6 Hz, 1H, CH_2), 5.35 (s, 5H, C_5H_5), 7.32 (m, 38H, Ph + C_6H_3).

(l) [Ru(C=CMeN=$NC_6H_3Cl_2$-2,4)(PPh_3)$_2$(η-C_5H_5)][BF_4] (12), from $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.274 mmol) and $[2,4\text{-}Cl_2C_6H_3N_2][BF_4]$ (71.5 mg, 0.274 mmol), as an orange powder (169 mg, 62%), m.p. 124–126°C (dec.) (Found: C, 60.14; H, 3.96; N, 2.66; $C_{50}H_{41}BCl_2F_4N_2P_2Ru$ calc: C, 60.62; H, 4.17; N, 2.83%). Infrared (Nujol): ν(C=C) + ν(N=N) 1592m; ν(BF) 1053s(br) cm^{-1}; other bands at 1482m, 1441s, 1438s, 1400w, 1368m, 1355m, 1318w, 1280w, 1245w, 1225w, 1172m, 1091s, 1038s, 999m, 824w, 788w, 745m, 696s, 672w cm^{-1}. ^1H NMR: δ ($CDCl_3$) 1.95 (s, 3H, Me), 5.42 (s, 5H, C_5H_5), 7.27 (m, 33H, Ph + C_6H_3). ^{13}C NMR: δ ($CDCl_3$) 7.55 (CH_3), 96.21 (C_5H_5), 118.35 (RuC=*C*), 127.13–134.58 (Ph + C_6H_3), 148.11, 157.66 (CCl).

(m) [Ru(C=CPhN=NC_6H_4OMe-4)(PPh_3)$_2$(η-C_5H_5)][BF_4] (13), from $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.631 mmol) and $[4\text{-}MeOC_6H_4N_2][BF_4]$ (140 mg, 0.631 mmol) as an orange powder (from dichloromethane/ethanol) (598 mg, 93%), m.p. 150–152°C (dec.) (Found: C, 65.69; H, 4.67; N, 2.78; $C_{56}H_{47}BF_4N_2OP_2Ru$ calc: C, 66.34; H, 4.67; N, 2.76%). Infrared (Nujol): ν(C=C) + ν(N=N) 1605s; ν(BF) 1060s(br) cm^{-1}; other bands at 1504s, 1483s, 1438s, 1421m, 1395s, 1341w, 1320m, 1301w, 1287w, 1250s, 1210m, 1190w, 1163m, 1152m, 1030s,

1001m, 975w, 951w, 934m, 902m, 858m, 840s, 810w, 791w, 750s, 723m, 696s, 679s cm^{-1}. ^1H NMR: δ ($CDCl_3$) 3.83 (s, 3H, OMe), 5.31 (s, 5H, C_5H_5), 7.32 (m, 39H, Ph + C_6H_4). ^{13}C NMR: δ ($CDCl_3$) 55.39 (OMe), 96.04 (C_5H_5), 113.67 (RuC=*C*), 123.72, 128.62–134.81 (Ph), 125.47, 148.01, 160.04, 160.97, N=*NC*$_6$; 364.54 (t, *J*(CP) 15.3 Hz, RuC).

(n) [Ru(C=CMeN=NC$_6$H$_4$OMe-4)(PPh$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] · 0.5EtOH (14) from Ru(C≡CMe)(PPh_3)$_2$(η-C_5H_5) (500 mg, 0.685 mmol) and [4-$MeOC_6H_4N_2$][BF_4] (152 mg, 0.685 mmol) as maroon crystals (from dichloromethane/ethanol) (520 mg, 77%), m.p. > 140°C (dec.) (Found: C, 63.47; H, 5.15; N, 2.74; $C_{51}H_{45}BF_4N_2OP_2Ru \cdot 0.5C_2H_6O$ calc: C, 63.55; H, 4.92; N, 2.85%). Infrared (Nujol): ν(C=C) + ν(N=N) 1608s; ν(BF) 1052s(br) cm^{-1}; other bands at 1505s, 1483s, 1442s, 1435s, 1420m, 1310m, 1296m, 1285w, 1252s, 1180s, 1175s, 1150m, 1000m, 938w, 876w, 847s, 839s, 825m, 810w, 785w, 770m, 749s, 723m, 697s, 685m, 660w cm^{-1}. ^1H NMR: δ ($CDCl_3$) 1.21 (t, *J*(HH) 7.1 Hz, 1.5H, CH_3CH_2), 1.91 (s, 3H, Me), 3.69 (q, *J*(HH) 7.1 Hz, 1H, CH_3CH_2), 3.85 (s, 3H, OMe), 5.37 (s, 5H, C_5H_5), 7.28 (m, 34H, Ph + C_6H_4).

Reactions of [Ru(C=CPhN=NPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (1)

(a) With triphenylphosphine. A mixture of **1** (200 mg, 0.192 mmol) and PPh_3 (52 mg, 0.20 mmol) was heated in refluxing benzene for 26 h. The solvent was removed in vacuo and a dichloromethane extract of the residue was filtered; addition of methanol to the filtrate and concentration afforded yellow crystals of Ru(C≡CPh)(PPh_3)$_2$(η-C_5H_5) (119 mg, 78%), identified on the basis of infrared and TLC (R_f) by comparison with an authentic sample.

(b) With 1,2-bis(diphenylphosphino)ethane. Similarly, **1** (200 mg, 0.192 mmol) and dppe (80 mg, 0.200 mmol) in refluxing benzene for 21 h afforded Ru(C≡CPh)(PPh_3)$_2$(η-C_5H_5) (80 mg, 53%) after a similar workup, which was identified as above.

(c) With water. Complex **1** (200 mg, 0.192 mmol) was heated in a refluxing mixture of tetrahydrofuran (15 ml) and water (5 ml) for 2.5 d. The solvent was removed in vacuo. Addition of ethanol to a dichloromethane extract of the residue and concentration afforded [Ru(CO)(PPh_3)$_2$(η-C_5H_5)][PF_6] as a beige powder (116 mg, 70%), m.p. 118–120°C (dec.) (Found: C, 58.49; H, 4.27. $C_{42}H_{35}F_6OP_3Ru$ calc: C, 57.82; H, 4.14%). Infrared (Nujol): ν(CO) 1980s(br), 1910m(br); ν(PF) 840s(br) cm^{-1}; other bands at 1589w, 1574w, 1482s, 1442s, 1436s, 1311w, 1262w, 1185w, 1170w, 1091s, 1072m, 1049w, 1028w, 999m, 929w, 742s, 721w, 695s cm^{-1}. (Infrared ($CHCl_3$): ν(CO) 1986 cm^{-1} cf. 1980 cm^{-1} in [Ru(CO)(PPh_3)$_2$(η-C_5H_5)][BPh_4] [12]). ^1H NMR: δ ($CDCl_3$) 4.99 (s, 5H, C_5H_5), 7.27 (m, 30H, Ph).

(d) With methanol. A solution of **1** (200 mg, 0.192 mmol) in methanol (10 ml) was refluxed for 5 d. The light yellow crystals which had deposited were collected, dried and identified as [Ru{C(OMe)CH_2Ph}(PPh_3)$_2$(η-C_5H_5)][PF_6] (46 mg, 25%), on the basis of their infrared and ^1H NMR spectra. TLC of the filtrate revealed 12 bands which were not investigated further.

(e) With carbon monoxide. A solution of **1** (200 mg, 0.192 mmol) in tetrahydrofuran (30 ml) was carbonylated in an autoclave (47 atm, 100°C, 16 h). After cooling to room temperature, the CO was released. The red solution had become light yellow. The solvent was removed on a rotary evaporator and a dichloromethane extract of the residue was filtered into stirred diethyl ether, precipitating

$[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (61 mg, 37%) which was identified by comparison of its IR spectrum with that of an authentic sample (vide supra). TLC of the filtrate revealed 10 bands which were not worked up further.

(f) With dihydrogen. A solution of **1** (200 mg, 0.192 mmol) in dichloromethane (20 ml) was hydrogenated in an autoclave (50 atm, 100°C, 22 h). After cooling to room temperature, the hydrogen was released and the solvent removed on a rotary evaporator. A dichloromethane extract of the residue was chromatographed (silica, 1/1 acetone/light petroleum), and afforded seven bands; the major band (yellow, R_f 0.92) was identified as $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (30 mg, 22%), after crystallisation from dichloromethane/light petroleum, on the basis of its infrared and ^1H NMR spectra.

(g) With iodomethane. A solution of **1** (200 mg, 0.192 mmol) in iodomethane (20 ml) was heated in an autoclave (47 atm N_2, 80°C, 20 h). After cooling to room temperature, the solution was reduced to dryness and a dichloromethane extract of the residue was filtered into diethyl ether, precipitating a light orange powder of $[Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)]X$ (nature of anion unknown, probably a mixture of I^- and I_3^-) (130 mg), m.p. 178–181°C (dec.) (Found: C, 59.10; H, 4.37%). Infrared (Nujol): ν(C=C) 1696m, 1672s cm^{-1}; other bands at 1592m, 1587w, 1482s, 1438s, 1418w, 1317w, 1189w, 1162w, 1092s, 1055s, 1030s, 1014m, 999s, 882m, 873m, 838w, 820w, 783m, 751m, 721w, 702s, 697s cm^{-1}. ^1H NMR: δ ($CDCl_3$) 1.93 (s, 3H, Me), 5.16 (s, 5H, C_5H_5), 7.05 (m, 35H, Ph). ^{13}C NMR: δ ($CDCl_3$) 12.18 (Me), 94.05 (C_5H_5), 127.57–135.28 (Ph). 17 mg of this salt was stirred in dichloromethane (5 ml) with NH_4PF_6 (5 mg, 0.031 mmol) for 30 min. The mixture was filtered into stirred ether, precipitating an orange powder identified as $[Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (12 mg) on the basis of its IR and ^1H NMR spectra.

(h) With $Mn(CH_2Ph)(CO)_5$. A mixture of **1** (250 mg, 0.240 mmol) and $Mn(CH_2Ph)(CO)_5$ (72 mg, 0.25 mmol) was heated in refluxing dichloromethane (10 ml) for 6 h. At this stage TLC indicated incomplete reaction, so more $Mn(CH_2Ph)(CO)_5$ (50 mg, 0.17 mmol) was added and the mixture refluxed for a further 21 h. The solution was cooled, the solvent was removed in vacuo, and a dichloromethane extract of the residue was chromatographed (silica; 1/1 acetone/light petroleum) affording five bands. The major band, purple (R_f 0.6), was crystallised from benzene/hexane as a purple powder, identified as $[Ru\{C{=}CPhN{=}NC_6H_4Mn(CO)_4\text{-}2\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (**15**) (52 mg, 18%), m.p. 138–140°C (dec.) (Found: C, 57.71; H, 3.83; N, 2.14; $C_{59}H_{44}F_6MnN_2O_4P_3Ru$ calc: C, 58.67; H, 3.67; N, 2.32%). Infrared (CH_2Cl_2): ν(CO) 2080m, 1999vs, 1959s cm^{-1}. ^1H NMR: δ ($CDCl_3$) 5.19 (s, 5H, C_5H_5), 7.27 (m, 39H, Ph + C_6H_4).

(i) With $[Me_3O][SbCl_6]$. A mixture of **1** (236 mg, 0.226 mmol) and $[Me_3O][SbCl_6]$ (121 mg, 0.226 mmol) was heated in refluxing chloroform (10 ml) for 18 h. The chloroform was removed in vacuo, extraction of the residue with dichloromethane, filtration, addition of ethanol and concentration afforded a yellow-brown powder which was recrystallised from dichloromethane/ethanol to give orange crystals of $[Ru(C{=}CPhN{=}NMePh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6][SbCl_6] \cdot EtOH$ (94 mg, 29%), m.p. 129–131°C (dec.) (Found: C, 48.58; H, 3.61; N, 1.74; $C_{56}H_{48}Cl_6F_6N_2P_3RuSb \cdot C_2H_6O$ calc: C, 48.46; H, 3.79; N, 1.95%). Infrared (Nujol): ν(N=N) + ν(C=C) 1609m, 1575m, 1564m; ν(PF) 840s(br) cm^{-1}; other bands at 1481m, 1441s, 1437s, 1418m, 1343m, 1263w, 1185w, 1161w, 1110w, 1090m, 1075w, 1025w, 999w, 933w, 886w, 775w, 742m, 718m, 692s cm^{-1}. ^1H NMR: δ ($CDCl_3$)

1.24 (t, J(HH) 7 Hz, 3H, CH_3CH_2), 1.57 (s, 3H, Me), 3.72 (q, J(HH) 7 Hz, 2H, CH_3CH_2), 5.29 (s, 5H, C_5H_5), 7.36 (m, 40H, Ph).

(j) With K[BH(CHMeEt)$_3$] (K-Selectride). A solution of **1** (200 mg, 0.192 mmol) in tetrahydrofuran (10 ml) was treated with *K*-Selectride (0.45 ml of a 0.5 *M* solution in tetrahydrofuran, 0.23 mmol). The solution was stirred for 16 h at which time two drops of ethanol were added. The solvent was then removed in vacuo and a dichloromethane extract of the residue was chromatographed (silica, 1/1 acetone/light petroleum), affording nine bands, one of which was identified as $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (4 mg, 3%) R_f 0.86.

(k) With sodium methoxide. A suspension of **1** (200 mg, 0.192 mmol) in methanol (10 ml) was treated with sodium methoxide (0.2 ml of a 1 *M* solution in MeOH, 0.2 mmol). The resulting mixture was refluxed 2.5 h. After cooling to room temperature, the light yellow precipitate which had deposited was collected, washed with methanol and dried, and identified as $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (26 mg, 17%). TLC of the filtrate revealed eight bands which were not investigated further.

(l) With $HPF_6 \cdot OEt_2$. A solution of **1** (204 mg, 0.196 mmol) in dichloromethane (20 ml) was treated with $HPF_6 \cdot OEt_2$ (3 drops, excess), and stirred for 16 h. The solvent was then removed in vacuo and a dichloromethane extract of the residue was chromatographed (silica, 2/1 acetone/light petroleum), affording 3 bands, the major one of which was red (R_f 0.7) isolated as an orange powder from dichloromethane/diethyl ether, and identified as $[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][PO_2F_2]$ (84 mg, 43%), m.p. 156–158°C (dec.) (Found: C, 66.10; H, 4.59; N, 2.78; $C_{55}H_{45}F_2N_2O_2P_3Ru$ calc: C, 66.20; H, 4.55; N, 2.81%). Infrared (Nujol): ν(C=C) + ν(N=N) 1590s; ν(PO) 1057s(br); ν(PF) 847m cm^{-1}; other bands at 1485m, 1439s, 1420s, 1310m, 1238m, 1197m, 1162w, 1155w, 1092s, 1080s, 1001m, 935w, 835w, 827w, 775w, 752s, 717s, 698s cm^{-1}. ^1H NMR: δ ($CDCl_3$) 5.33 (s, 5H, C_5H_5), 7.29 (m, 40H, Ph).

The following FAB mass spectra were obtained (m/z, based on ^{102}Ru or ^{192}Os, assignment, relative intensity). Peaks marked with * are at the centre of multiplets which consist of the designated ion together with ions related by the loss of one or two H atoms.

(a) [Ru{C=CMeN=N(C$_6$H$_4$NO$_2$-4)}(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (***10***). 880, $[M]^+$, 15; 730, $[M - (N_2C_6H_4NO_2)]^+$, 7; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$, 4; 618*, $[M - PPh_3]^+$, 8; 428*, $[Ru(PPh_3)(C_5H_5) - H]^+$, 100.

(b) [Ru{C=C(C$_6$F$_5$)N=N(C$_6$H$_3$Me$_2$-3,4)}(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (***8***). 1015, $[M]^+$, 3; 896, $[M - (NC_6H_3Me_2)]^+$, 2; 882, $[M - (N_2C_6H_3Me_2)]^+$, 33; 863, $[882 - F]^+$, 4; 753*, $[M - PPh_3]$, 6; 691*, $[Ru(PPh_3)_2(C_5H_5)]^+$, 5; 634, $[M - PPh_3 - (NC_6H_3Me_2)]^+$, 5; 620, $[M - PPh_3 - (N_2C_6H_3Me_2)]^+$, 23; 601, $[620 - F]^+$, 7; 543, $[Ru(C_2C_6F_5)(PPh_2)(C_5H_5)]^+$, 80; 524, $[543 - F]^+$, 10; 429–427, $[Ru(PPh_3 - nH)(C_5H_5)]^+$, 100; 358*, $[Ru(C_2C_6F_5)(C_5H_5)]^+$, 23; 352, $[Ru(PPh_2)(C_5H_5)]^+$; 287*, $[Ru(PPh_2)]^+$, 33; 244*, $[RuPh(C_5H_5)]^+$, 52; 210*, $[RuPPh]^+$, 21; 167, $[Ru(C_5H_5)]^+$, 20.

(c) [Os(C=CPhN=NPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (***5***). 1141*, $[M + \text{matrix}]^+$, 17; 987*, $[M]^+$, 7; 959*, $[M - N_2]^+$, 12; 879*, $[1141 - PPh_3]^+$, 42; 825*, –, 10; 809*, $[Os(CO)(PPh_3)_2(C_5H_5)]^+$, 9; 781, $[Os(PPh_3)_2(C_5H_5)]^+$, 33; 757*, –, 12; 725*, $[M - PPh_3]^+$, 32; 697*, $[959 - PPh_3]^+$, 24; 620*, $[Os(C_2Ph)(PPh_3)(C_5H_5)]^+$, 64; 519*, $[Os(PPh_3)(C_5H_5)]^+$, 80; 442*, $[Os(PPh_2)(C_5H_5)]^+$, 100.

(d) [Ru{C=CPhN=NC$_6$H$_4$Mn(CO)$_4$}(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (***15***). 1063, $[M]^+$,

51.3; 1035, $[M - CO]^+$, 3.2; 979, $[M - 3CO]^+$, 3.2; 951, $[M - 4CO]^+$, 6.4; 923, $[M - 4CO - N_2]^+$, 5.1; 897, $[M - Mn(CO)_4 + H]^+$, 11.5; 869, $[897 - N_2]^+$, 4.5; 792, $[897 - N_2Ph]^+$, 50; 719, $[Ru(CO)(PPh_3)_2(C_5H_5)]^+$, 37.2; 691*, $[Ru(PPh_3)_2(C_5H_5)]^+$, 24.4; 661, $[923 - PPh_3]^+$?, 18.6; 529, $[897 - N_2Ph - PPh_3]^+$, 29.5; 453, $[Ru(C_2Ph)(PPh_2)(C_5H_5)]^+$, 55; 429*, $[Ru(PPh_3)(C_5H_5)]^+$, 100.

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