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Nucleophilic Addition to Complexes of $(Ph_2P)_2C{=}CH_2$ as a Route to Functionalized, Redox-Active Ruthenium(II)−Diphosphine Complexes

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The ligand $(Ph_2P)_2C{=}CH_2$ (dppen) reacts with $[RuCl_2(PPh_3)_3]$ in CH_2Cl_2 to give *trans*-$[RuCl_2(dppen)_2]$, **1**. Complex **1** has reversible Ru(II)/Ru(III) electrochemistry, and on treatment with $NOBF_4$, **1** affords $[RuCl_2(dppen)_2]BF_4$, $\mathbf{1}^+$. Refluxing solutions of **1** in chlorobenzene affords *cis*-$[RuCl_2(dppen)_2]$, **2**. With excess RNH_2 in chlorobenzene or toluene, **1** reacts to give functionalized diphosphine complexes of general formula *trans*-$[RuCl_2(\{Ph_2P\}_2CHCH_2NHR)_2]$ (R: $PhCH_2$, **3a**; $[CH_2]_3NH_2$, **3b**; *n*-octyl, **3c**; *R*-α-CH(Me)Ph, **3d**; $[CH_2]_3Si(OEt)_3$, **3e**) characterized principally by a small upfield shift in their $^{31}P\{^1H\}$ NMR spectra compared to that of **1** and by their distinctive ^1H NMR spectra. Complex **3b**·4MeOH crystallizes in the space group $P\bar{1}$ with $a = 11.448(6)$ Å, $b = 13.10(1)$ Å, $c = 11.178(7)$ Å, $\alpha = 93.16(6)°$, $\beta = 99.51(5)°$, $\gamma = 92.19(5)°$, $V = 1648(2)$ Å^3, and $D_{calcd} = 1.250$ g cm^{-3} for $Z = 1$. Complex **3e** reacts with the surface hydroxyl groups of indium-doped tin oxide (ITO) electrodes, to give monolayers of anchored, redox-active Ru(II)−diphosphine complexes, characterized by cyclic voltammetry. The modified electrodes are stable to repetitive cycling over the Ru(II)/Ru(III) redox wave in acetonitrile−tetraethylammonium tetrafluoroborate and in aqueous buffer (pH 8). With anodized Pt electrodes, however, **3e** reacts to form multilayers. Reaction of **1** with secondary amines is more sluggish than reaction with primary amines, and only adducts with pyrrolidine (**3f**) and morpholine (**3g**; impure) were isolated. With $LiC{\equiv}C(CH_2)_3CH_3$, **1** reacts to give *trans*-$[Ru(C{\equiv}CR)_2(\{Ph_2P\}_2CHCH_2C{\equiv}CR)_2]$ (R = *n*-butyl, **5**); acetylide nucleophiles displace the chloride ligands as well as adding to the dppen double bonds of **1**. Other carbanions fail to react with **1**. The *cis* complex **2** reacts with a limited range of primary amines, to afford *cis*-$[RuCl_2(\{Ph_2P\}_2CHCH_2NHR)_2]$ (R: *n*-hexyl, **4a**; $[CH_2]_3Si[OEt]_3$, **4b**). However, **4b** was too insoluble for electrode derivatization. The “half-sandwich” complex $[CpRuCl(dppen)]$ (**6**; Cp = η^5-C_5H_5) also reacts with RNH_2 to give $[CpRuCl(\{PPh_2\}_2CHCH_2NHR)]$ (R: $-[CH_2]_3NH_2$, **7a**; $-CH_2Ph$, **7b**).

Covalent anchoring of metal complexes to surfaces is a topic of considerable interest in both catalysis[1] and electrochemistry,[2−5] although these two fields have developed independently. In the former field, the chief interest is in attempting to combine the advantages of homogeneous catalysis (high selectivities, high activities) and heterogeneous catalysis (ease of separation of catalyst from products)[1] by fixing complexes active in homogeneous catalysis to heterogeneous supports; the metal centers involved are usually platinum metal−phosphine complexes. The approach employed is either to make a suitable complex of a ligand such as $Ph_2P(CH_2)_3Si(OR)_3$ and then react this with an oxide surface or to derivatize the oxide first with the siloxyphosphine ligand and subsequently carry out an exchange reaction with a labile metal complex. A major problem in this field has been that, under the conditions commonly required for effective catalysis, ligand exchange reactions lead to leaching of the metal centers from the oxide-anchored ligands. The use of multidentate ligands functionalized with anchoring groups might limit this, but few such ligands have been described, probably because of synthetic difficulties.[6]

In electrochemistry, the anchoring of a monolayer of a redox-active metal complex to an electrode surface offers the possibility of controlling the reactivity of the electrode more precisely than can be achieved simply by controlling its potential. Such “modified electrodes” have been widely studied in electrocatalytic reactions and in various sensing applications.[2,4] Interest was also stimulated by the possibility of solar harvesting using silicon covered with monolayers of photoactive species or simply protecting semiconductors from photocorrosion.[7,8] The first deliberate modification of an electrode was achieved using a Pt(IV) complex of an alkene-functionalized pyridine ligand.[9] More recently, the study of long-chain alkanethiols self-assembled on gold, including some metal complex-terminated examples, has become a very active area.[10−12] The metal centers employed are usually classical redox-active species such as metal porphyrins and metal phthalocyanines, $[M(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine), ferrocenes, etc. Although metal−phosphine complexes are important in homogeneous catalysis, their application to monolayer-modified electrodes has not so far attracted much attention, probably since platinum metal complexes of ligands such as $Ph_2P(CH_2)_3Si(OR)_3$ do not usually have reversible redox processes.

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(1) Iwasawa, Y. Inorganic Oxide-attached Metal Catalysts. In *Tailored Metal Catalysts*; Iwasawa, Y., Ed.; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1986.

(2) Abruña, H. D. *Coord. Chem. Rev.* **1988**, *86*, 135.

(3) Miller, J. S. *Chemically-Modified Surfaces in Catalysis and Electrocatalysis*; American Chemical Society: Washington, DC, 1982.

(4) Murray, R. W. *Molecular Design of Electrode Surfaces*; John Wiley: New York, 1992.

(5) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135.

(6) Fox, M. A.; Chandler, D. A.; Wang, P. *Macromolecules* **1991**, *24*, 4626.

(7) Anderson, S.; Constable, E. C.; Dare-Edwards, M. P.; Goodenough, J. B.; Hamnett, A.; Seddon, K. R.; Wright, R. D. *Nature (London)* **1979**, *280*, 5723.

(8) Wrighton, M. S. *Acc. Chem. Res.* **1979**, *12*, 303.

(9) Lane, R. F.; Hubbard, A. T. *J. Phys. Chem.* **1973**, *73*, 1401.

(10) Chidsey, C. E. *Science* **1991**, *251*, 919.

(11) Fox, M. A. *Acc. Chem. Res.* **1992**, *25*, 569.

(12) Hickman, J. J.; Laibinis, P. E.; Auerbach, D. I.; Zou, C.; Gardner, T. J.; Whitesides, G. M.; Wrighton, M. S. *Langmuir* **1992**, *8*, 357.

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The ligand 1,1-bis(diphenylphosphino)ethene (dppen) undergoes ready nucleophilic addition when chelated to metal centres such as M(CO)$_4$ (M = Cr, Mo, W),[13−15] PtMe$_2$ and PtIMe$_3$,[16] MX$_2$ (M = Pd, Pt; X = Cl, I; M = Pd, X = OAc),[17−19] and NiCl$_2$.[20] The driving force for the reaction has not been established with certainty but is probably a combination of relief of angle strain at the carbon adjacent to the donor atoms and polarization of the double bond by coordination of the phosphines. Indirect evidence for the latter is that the reactivity of the ligand depends markedly upon the particular metal center to which it is coordinated. Thus, the least reactive examples, [M(CO)$_4$(dppen)], react with acetylide anions and, on heating, with amines and hydrazines (in large excess).[13−15] The most reactive example so far, [Pd(OAc)$_2$(dppen)], reacts readily with primary alcohols, extremely weak nucleophiles, in CH$_2$Cl$_2$ solution at room temperature.[17,19]

Coordinatively saturated complexes of Ru(II) have the twin advantages of chemical stability and accessible, reversible Ru(III)/Ru(II) redox processes.[21,22] We have therefore employed nucleophilic addition to dppen complexed to Ru(II) to afford complexes suitable for modification of electrode surfaces with monolayers, using cyclic voltammetry to characterize the anchored complexes. Herein we report the syntheses and characterization of *trans*-[RuCl$_2$(dppen)$_2$] (**1**) and *cis*-[RuCl$_2$(dppen)$_2$] (**2**), their reactivity with primary and secondary amines, and the derivatization of electrode surfaces with the amine adduct *trans*-[RuCl$_2$({Ph$_2$P}$_2$CHCH$_2$NH{CH$_2$}$_3$Si{OEt}$_3$)$_2$] (**3e**). We also describe some attempts to extend this chemistry to the "half-sandwich" complex [CpRuCl(dppen)] (**6**; Cp = η^5-C$_5$H$_5$).[23] A preliminary account of some aspects of the work has appeared.[24]

Experimental Section

General Considerations. Reactions were carried out under nitrogen, using Schlenk-line techniques for transfer of organolithium reagents. Reaction solvents were reagent grade and were dried by distillation from CaH$_2$ (CH$_2$Cl$_2$) or sodium benzophenone ketyl (thf, diethyl ether, heptane). Perdeuterated solvents for NMR studies were used as received. The ligand dppen was prepared by the published method[25] (tetrahydrofuran was used instead of benzene as solvent for Cl$_2$C=CH$_2$), as were [RuCl$_2$(PPh$_3$)$_3$][26] and [CpRu(dppen)Cl] (Cp = η^5-C$_5$H$_5$).[23] Tetrabutylammonium tetrafluoroborate (TBAT) was prepared from the bromide (Lancaster Synthesis) and 50% HBF$_4$ (Fluka) in water and recrystallized twice from acetone−water. It was dried at 60 °C *in vacuo*. Solvents were dried by standard techniques.[27] The following were used as received: KO^{t}Bu, 18-crown-6, CDCl$_3$.

Characterization. Microanalyses were performed in house by Mr. Steve Apter; the presence of solvent of crystallization inferred from the analytical results was in all cases confirmed by ^{1}H NMR spectroscopy. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker WM 250 MHz spectrometer at 250 and 101 MHz, respectively, in CDCl$_3$ unless otherwise stated; broad-band proton decoupling and line broadening (8 Hz) were employed for ^{31}P NMR spectra. Some ^{1}H NMR spectra were recorded at 400 MHz on a Bruker AMX spectrometer. Chemical shifts are reported in ppm (relative to TMS [^{1}H] or 85% H$_3$PO$_4$ [^{31}P]). Low-resolution fast-atom-bombardment mass spectra (FAB MS) of the complexes, in 3-nitrobenzyl alcohol matrices, were recorded with a VG 7070E instrument in positive-ion mode. Electrochemical experiments were conducted using a Sycopel Scientific Scanning Ministat potentiostat and Lloyd PL3 X-Y-t recorder. A three-electrode one-compartment cell, with the reference electrode separated by a glass frit and a Luggin capillary, was employed. For solution studies, working electrodes were Pt disks (Sycopel). Throughout this paper, a CH$_2$Cl$_2$ solution of TBAT was used as electrolyte for solution studies except where otherwise stated. Modified electrodes were either indium-doped tin oxide (ITO)-coated glass (a gift from Pilkington Group Research, Lathom, U.K.) or anodized Pt disks. ITO-coated glass was cleaned in 0.1% NaOH solution. The slides were dried, briefly (15−30 s) exposed to "pirhana solution" (30% H$_2$O$_2$/H$_2$SO$_4$; *care*! *explosive when mixed with organic material*), rinsed thoroughly with triply-distilled water, and dried at 60 °C. They were then refluxed in propan-2-ol and dried before derivatization. The Pt disks were anodized by potential cycling in aqueous sulfuric acid.[28] They were then washed with triply-distilled water and dried at 60 °C before derivatization. The counter electrode was a Pt gauze, and the reference electrode was an Ag wire in 0.01M AgNO$_3$/CH$_3$CN/0.2 M Bu$_4$NBF$_4$ (CH$_2$Cl$_2$) or a commercial saturated calomel electrode (CH$_3$CN). Because different reference electrodes and electrolytes were employed for solution and modified electrode voltammetry, all potentials in this paper are quoted with respect to the ferrocene/ferrocenium couple, which was routinely monitored after each set of voltammetric measurements. Its potential occurred at +0.19 V *vs* the Ag/Ag$^+$ electrode (CH$_2$Cl$_2$) and +0.58 V *vs* SCE (CH$_3$CN).

Syntheses. (a) *trans*-[RuCl$_2$(dppen)$_2$] (1). To [RuCl$_2$(PPh$_3$)$_3$] (4.0 g, 4.18 mmol) in CH$_2$Cl$_2$ (20 cm^3) was added dppen (3.37 g, 8.5 mmol), and the mixture was stirred at room temperature for 3 h. The orange product was filtered off, washed with CH$_2$Cl$_2$ (2 cm^3) and then Et$_2$O (20 cm^3), and dried *in vacuo*. Yield: 3.42 g, 85%. A further quantity could be obtained by adding EtOH to the CH$_2$Cl$_2$ mother liquor. Anal. Calcd for C$_{52}$H$_{44}$Cl$_2$P$_4$Ru·CH$_2$Cl$_2$: C, 60.64; H, 4.42. Found: C, 60.52; H, 4.40. FAB MS, *m/z*: 965 (100) M$^+$; 930 (27) [M − Cl]$^+$; 894 (16) [M − Cl − HCl]$^+$. IR data (cm^{-1}): 328 (m) ($\nu_{\text{Ru−Cl}}$). Electronic spectral data, $E_{\max}/10^{-3}$ cm^{-1} (ϵ/L mol^{-1} cm^{-1}) (CH$_2$Cl$_2$): 24.15 (2240). ^{31}P NMR: δ 14.7 (s). ^{1}H NMR data: δ 7.43−7.08 (40H, Ph), 6.12 (4H, quintet, C=C**H$_2$**). Ru(II)/Ru(III) $E_{1/2}$: +0.01 V.

(b) *trans*-[RuCl$_2$(dppen)$_2$]BF$_4$ (1$^+$). To **1** (0.60 g, 0.62 mmol) in CH$_2$Cl$_2$ (40 cm^3) at 0 °C was added NOBF$_4$ (0.073 g, 0.62 mmol) with stirring and with N$_2$ bubbling to displace NO. After 2 h, the solvent volume was reduced *in vacuo* and the product was precipitated with diethyl ether, filtered off, and dried *in vacuo*. Yield: 0.60 g, 92%. Anal. Calcd for C$_{52}$H$_{44}$BCl$_2$F$_4$P$_4$Ru·CH$_2$Cl$_2$: C, 56.01; H, 4.08. Found: C, 56.50; H, 4.29. FAB MS, *m/z*: 965 (100) M$^+$; 930 (20) [M − Cl]$^+$; 894 (8) [M − Cl − HCl]$^+$. Selected IR data (cm^{-1}): 1058 (s) (BF$_4^-$). Electronic spectral data, $E_{\max}/10^{-3}$ cm^{-1} (CH$_2$Cl$_2$): 14.16, 20.8 (br, sh), 24.10.

(c) Isomerization of 1 to *cis*-[RuCl$_2$(dppen)$_2$] (2). **1** (3.24 g, 3.35 mmol) in chlorobenzene (150 cm^3) was heated to reflux for 16 h under nitrogen; samples were withdrawn periodically and the ^{31}P{^{1}H} NMR spectra recorded. Once no further reaction occurred, solvent was removed *in vacuo*. The product was extracted with MeOH (200 cm^3), the extract was filtered, the filtrate was evaporated to dryness, and the

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(13) Cooper, G. R.; McEwan, D. M.; Shaw, B. L. *Inorg. Chim. Acta* **1986**, *122*, 207.

(14) Hassan, F. S. M.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 89.

(15) Haupt, H.-J.; Kleineberg, E.; Flörke, U. *Z. Anorg. Allg. Chem.* **1993**, *619*, 869.

(16) Hassan, F. S. M.; Higgins, S. J.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 3011.

(17) King, G.; Higgins, S. J.; Hopton, A. *J. Chem. Soc., Dalton Trans.* **1992**, 3403.

(18) Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1989**, 1527.

(19) Herring, A. M.; Higgins, S. J.; Jacobsen, G. B.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1986**, 882.

(20) Brunner, H.; Limmer, S. *J. Organomet. Chem.* **1991**, *417*, 173.

(21) Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1037.

(22) Champness, N. R.; Levason, W.; Pletcher, D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1992**, 3243.

(23) Brown, M. P.; Burns, D.; Das, R.; Dolby, P. A.; Harding, M. M.; Jones, R. W.; Robinson, E. J.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1991**, 351.

(24) Higgins, S. J.; McCart, M. K.; McElhinney, M.; Nugent, D. C.; Pounds, T. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2129.

(25) Colquhoun, I. J.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1982**, 1915.

(26) Hallman, P. S.; Stevenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.

(27) Perrin, D. D.; Armarego, W. L. F. *The Purification of Laboratory Compounds*, 3rd ed.; Pergamon: Oxford, U.K., 1988.

(28) Casado, C. M.; Morán, M.; Losada, J.; Cuadrado, I. *Inorg. Chem.* **1995**, *34*, 1668.

residue was dried *in vacuo*. The complex was stored in the dark. Yield: 1.04 g, 32%. Anal. Calcd for $C_{52}H_{44}Cl_2P_4Ru\cdot H_2O$: C, 63.55; H, 4.72. Found: C, 63.33; H, 4.60. FAB MS, *m/z*: 965 (100) M^+; 930 (27) $[M - Cl]^+$; 894 (16) $[M - Cl - HCl]^+$. Selected IR data (cm^{-1}): 3400 (br) (H_2O); 300 (w) and 270 (w) (ν_{Ru-Cl}). Electronic spectral data, $E_{max}/10^{-3}$ cm^{-1} (CH_2Cl_2): 22.73 (sh), 27.17. ^{31}P NMR: δ 13.84 (s, P−*trans*-P), −3.57 (s, P−*trans*-Cl). Selected ^1H NMR data: δ 8.25 (m, 4H, aromatic H), 7.5−6.7 (m, 28H, aromatic H), 6.52 (dt, 8H, aromatic H), 6.02 (4H, complex m, $C{=}C\mathbf{H}_2$). Ru(II)/Ru(III) $E_{1/2}$ (CH_2Cl_2/0.2 M TBAT): +0.41 V.

(d) Primary Amine Adducts of 1: 3a−e. 1 (0.2 g) was suspended in toluene (10 cm^3), and the appropriate RNH_2 (1.0 cm^3) was added. The mixture was stirred for 16 h. The orange suspension dissolved to give a yellow solution. The toluene was removed under reduced pressure, to *ca.* 5 cm^3, and the product was left to crystallize at room temperature for 48 h (R = $-CH_2Ph$ (**3a**)). Alternatively, the product was precipitated with methanol (R = $-(CH_2)_3NH_2$ (**3b**), *n*-octyl (**3c**), *R*-α-CH(Me)Ph (**3d**)) or dry diethyl ether (R = $-(CH_2)_3Si(OEt)_3$ (**3e**)). The product was filtered off, washed with a little diethyl ether or methanol, and dried *in vacuo*.

3a. Yield: 78%. Anal. Calcd for $C_{66}H_{62}Cl_2N_2P_4Ru\cdot 0.5C_7H_8$: C, 68.23; H, 5.39; N , 2.29. Found: C, 68.20; H, 5.46; N, 2.05. FAB MS, *m/z*: 1178 M^+; 1143 $[M - Cl]^+$; 1107 $[M - Cl - HCl]^+$. ^{31}P NMR: δ 12.95 (s). Selected ^1H NMR data: δ 5.49 (2H, m, $P_2C\mathbf{H}CH_2$), 3.62 (4H, s, $NHC\mathbf{H}_2Ph$), 3.11 (2H, m, $P_2CHC\mathbf{H}_2$, J_{HH} 6.4 Hz, apparent J_{PH} 5.85 Hz), 1.53 (br s, N**H**). Ru(II)/Ru(III) $E_{1/2}$: −0.02 V.

3b. Yield: 52%. Anal. Calcd for $C_{58}H_{64}Cl_2N_4P_4Ru\cdot 2H_2O$: C, 60.63; H, 5.97; N, 4.88. Found: C, 61.02; H, 5.77; N, 4.82. FAB MS, *m/z*: 1112 M^+; 1077 $[M - Cl]^+$; 1042 $[M - Cl - HCl]^+$. Electronic spectral data, $E_{max}/10^{-3}$ cm^{-1} (ϵ/L mol^{-1} cm^{-1}) (CH_2Cl_2): 20.58 (110), 23.92 sh (210), 31.85 sh (2370). ^{31}P NMR: δ 10.70 (s). Selected ^1H NMR data: δ 5.38 (2H, m, $P_2C\mathbf{H}CH_2$) 2.96 (4H, m, $P_2CHC\mathbf{H}_2$), 2.55 (4H, t, J_{HH} 6.0 Hz, $-NHC\mathbf{H}_2CH_2$), 2.43 (4H, t, J_{HH} 6.0 Hz, $-CH_2C\mathbf{H}_2NH_2$), 1.41 (4H, qnt, $-CH_2C\mathbf{H}_2CH_2-$), 1.25 (*ca.* 10H, br s, N**H**, $\mathbf{H}_2O$). Ru(II)/Ru(III) $E_{1/2}$: 0.00 V.

3c. Yield: 56%. Anal. Calcd for $C_{68}H_{82}Cl_2N_2P_4Ru\cdot 2MeOH$: C, 65.30; H, 7.05; N, 2.18. Found: C, 65.01; H, 6.90; N, 2.08. FAB MS, *m/z*: 1222 (100) M^+; 1187 (31) $[M - Cl]^+$; 1147 (11) $[M - Cl - HCl]^+$. ^{31}P NMR: δ 12.70 (s). Selected ^1H NMR data: δ 5.45 (2H, m, $P_2C\mathbf{H}CH_2$), 3.02 (4H, m, $P_2CHC\mathbf{H}_2$), 2.40 (4H, t, J_{HH} 6.7 Hz, $NHC\mathbf{H}_2C_7H_{15}$), 1.40−1.19 (24H, overlapping m's, $NHCH_2C_6\mathbf{H}_{12}CH_3$), 0.86 (6H, t, J_{HH} 6.6 Hz, $NHC_7H_{14}C\mathbf{H}_3$). Ru(II)/Ru(III) $E_{1/2}$: −0.01 V.

3d. Yield: 57%. Anal. Calcd for $C_{68}H_{66}Cl_2N_2P_4Ru\cdot H_2O$: C, 66.66; H, 5.60; N, 2.29. Found: C, 66.46; H, 5.59; N, 2.15. FAB MS, *m/z*: 1206 (100) M^+; 1171 $[M - Cl]^+$; 1135 $[M - Cl - HCl]^+$. ^{31}P NMR: δ 9.14 (m). Selected ^1H NMR data: δ 5.45 (2H, m, $P_2C\mathbf{H}CH_2$), 3.57 (2H, quartet, J_{HH} 6.48 Hz, $NHC\mathbf{H}(CH_3)Ph$), 2.97 (4H, br m, $P_2CHC\mathbf{H}_2$), 1.54 (br s, N**H** and $\mathbf{H}_2O$), 1.14 (6H, d, $NHCH(C\mathbf{H}_3)Ph$).

3e. Yield: 65%. Anal. Calcd for $C_{70}H_{90}Cl_2O_6N_2P_4RuSi_2$: C, 59.78; H, 6.45; N, 1.99. Found: C, 58.20; H, 6.40; N, 2.15. FAB MS, *m/z*: 1409 (100) M^+; 1374 (46) $[M - Cl]^+$. ^{31}P NMR: δ 10.89 (s). Selected ^1H NMR data: δ 5.40 (m, $P_2C\mathbf{H}CH_2$), 3.70 (q, J_{HH} 6.9 Hz, $Si(OC\mathbf{H}_2CH_3)_3$), 3.00 (br m, $P_2CHC\mathbf{H}_2$), 2.40 (t, $-NHC\mathbf{H}_2CH_2CH_2Si$), 1.60 (br, N**H**), 1.41 (br m, $-NHCH_2C\mathbf{H}_2CH_2Si$), 1.28 (t, $Si(OCH_2C\mathbf{H}_3)_3$), 0.47 (m, $-NHCH_2CH_2C\mathbf{H}_2Si$). Ru(II)/Ru(III) $E_{1/2}$: +0.03 V.

(e) Secondary Amine Adducts of 1: 3f,g. 1 (0.2 g) was dissolved/suspended in toluene (10 cm^3), and the amine (3 cm^3) was added. The mixture was stirred for 16 h (pyrrolidine, **3f**) or refluxed gently for 30 min (morpholine, **3g**). Solvent was removed under reduced pressure, and the product was precipitated by addition of methanol. It was filtered off, washed with methanol, and dried *in vacuo*.

3f. Yield: 69%. Anal. Calcd for $C_{60}H_{62}Cl_2N_2P_4Ru$: C, 65.10; H, 5.65; N, 2.53. Found: C, 64.60; H, 5.69; N, 2.41. FAB MS, *m/z*: 1107 (100) M^+; 1072 $[M - Cl]^+$; 1036 $[M - Cl - HCl]^+$. ^{31}P NMR: δ 11.85 (s). Selected ^1H NMR data: δ 5.49 (2H, m, $P_2C\mathbf{H}CH_2$), 2.84 (4H, m, $P_2CHC\mathbf{H}_2$), 2.44 (8H, br s, pyrrolidine ring H), 1.80 (8H, br s, pyrrolidine ring H).

3g. Yield: 79%. FAB MS, *m/z*: 1139 M^+; 1104 $[M - Cl]^+$, 1068 $[M - Cl - HCl]^+$. ^{31}P NMR: δ 12.24 (s). Selected ^1H NMR data: δ 5.52 (2H, m, $P_2C\mathbf{H}CH_2$).

(f) Primary Amine Adducts of 2. 4a. To a mixture of chlorobenzene (20 cm^3) and **2** (0.271 g, 0.279 mmol) in a foil-covered flask was added *n*-hexylamine (0.5 cm^3, 9.2 mmol) with stirring. After 16 h, solvent was removed *in vacuo*, and the yellow oil remaining was triturated with hexanes. The product was filtered off and dried *in vacuo*.

4b. To a mixture of dry toluene (20 cm^3) and **2** (0.296 g, 0.307 mmol) in a foil-covered flask under N_2 was added (3-aminopropyl)triethoxysilane (1.6 cm^3, 6.7 mmol) with stirring. After 24 h, the solvent was evaporated off and the yellow oil remaining was triturated with hexanes. The product was filtered off and dried *in vacuo*.

4a. Yield: 0.23 g, 63%. ^{31}P NMR: δ 12.41, 27.27 (two t, AA′XX′; $|J_{AX} + J_{AX'}|$ = 59 Hz). Selected ^1H NMR data: δ 7.99 (m, br, Ph), 7.84 (m, Ph), 7.58 (m, Ph), 7.29 (m, Ph), 7.11 (m, Ph), 6.71 (m, Ph) (total: 40H), 5.32 (2H, br, $P_2C\mathbf{H}CH_2$), 2.30 (6H, br, overlapping m's, $P_2CHC\mathbf{H}_2$ and N**H**), 1.60 (4H, br m, $-NHC\mathbf{H}_2C_4H_8Me$), 1.25 (m, 16H, $-NHCH_2C_4\mathbf{H}_8Me$), 0.81 (m, 6H, $-NHCH_2C_4H_8\mathbf{Me}$).

4b. Yield: 0.28 g, 65%. FAB MS, *m/z*: 1406 (85) M^+; 1371 (100) $[M - Cl]^+$; 1335 (12) $[M - Cl - HCl]^+$. ^{31}P NMR (obtained on crude product; see Results and Discussion): δ 12.30, 27.23 (two t, AA′XX′; $|J_{AX} + J_{AX'}|$ = 58 Hz). ^1H NMR data (obtained on crude product; see Results and Discussion): δ 8.08 (br m, Ph), 7.89 (br m, Ph), 7.61 (br m, Ph), 7.28 (m, Ph), 6.75 (br m, Ph), 5.38 (br m, $P_2C\mathbf{H}CH_2$), 3.78 (m, J_{HH} 5.8 Hz, $-Si\{OC\mathbf{H}_2CH_3\}_3$), 2.67 (t, J_{HH} 7.1 Hz, $-NHC\mathbf{H}_2CH_2-$), 2.20 (complex m, $P_2CHC\mathbf{H}_2$), 1.53 (m, $-NHCH_2C\mathbf{H}_2CH_2-$), 1.22 (m, $-Si\{OCH_2C\mathbf{H}_3\}_3$), 0.62 (m, $-C\mathbf{H}_2Si-$).

(g) Acetylide Adduct 5. 1 (0.3 g, 0.31 mmol) was dissolved/suspended in THF (10 cm^3). A solution of the acetylide (prepared from hexyne [0.229 g, 2.78 mmol] and *n*-BuLi [1.17 mL of 1.6 M; 1.87 mmol]) in THF (2 cm^3) was added *via* cannula at −78 °C, and the mixture was then allowed to warm to room temperature. The color lightened, and the suspended complex dissolved. Solvents were removed under reduced pressure, and the resulting light brown oil was triturated with MeOH at 0 °C. The tan solid **5** was filtered off and dried *in vacuo*. Yield: 0.15 g, 42%. Anal. Calcd for $C_{72}H_{78}Cl_2N_2P_4Ru\cdot 0.25CH_2Cl_2$: C, 72.93; H, 7.06. Found: C, 72.08; H, 6.47. FAB MS, *m/z*: 1221 (7) M^+; 1139 (67) $[M - HC{\equiv}CR]^+$; 1057 (100) $[M - 2HC{\equiv}CR]^+$; 975 (15) $[M - 3HC{\equiv}CR]^+$. ^{31}P NMR: δ 8.01 (s). Selected ^1H NMR data: δ 7.90, 7.62, 7.22, 7.06 (m's, Ph), 5.50 (m, apparent J_{PH} 6.0 Hz, J_{HH} 4.9 Hz, $P_2C\mathbf{H}CH_2$), 3.49 (d, J_{HH} 4.9 Hz, $P_2CHC\mathbf{H}_2$), 2.25, 2.02 (br m's, $C{\equiv}CC\mathbf{H}_2R$), 1.52 (overlapping m's, $C{\equiv}CCH_2C\mathbf{H}_2CH_2CH_3$), 1.28 (overlapping m's, $C{\equiv}CCH_2CH_2C\mathbf{H}_2CH_3$), 0.81 and 0.73 (overlapping t's, J_{HH} 6.9 Hz, $-CH_2C\mathbf{H}_3$).

(h) Addition of Primary Amines to [CpRu(dppen)Cl] (6). To [CpRu(dppen)Cl] (**6**) (0.1 g, 0.17 mmol) in toluene (15 cm^3) was added $H_2N(CH_2)_3NH_2$ (**7a**; 1 cm^3) or $PhCH_2NH_2$ (**7b**; 0.043 g, 0.4 mmol). The mixture was allowed to stand for 16 h. Solvent was removed *in vacuo*, and the mixture was triturated with MeOH (**7a**) or Et_2O (**7b**). The product was filtered off and dried *in vacuo*. Yields: 0.018 g, 22% (**7a**); 0.017 g, 20% (**7b**).

7a. Anal. Calcd for $C_{34}H_{37}ClN_2P_2Ru$: C, 60.75; H, 5.56; N, 4.17. Found: C, 58.41; H, 5.63; N, 4.62. FAB MS, *m/z*: 673 (50) M^+; 637 (20) $[M - Cl]^+$. ^{31}P NMR: δ 33.2 (s). Selected ^1H NMR data 7.82 (m, Ph) and 7.40 (m, Ph), 4.89 (s, $C_5\mathbf{H}_5$), 4.83 (complex m, $P_2C\mathbf{H}CH_2$), 2.90 (t, J_{HH} 6.3 Hz, $HNC\mathbf{H}_2(CH_2)_2NH_2$), 2.70 (complex m, $P_2CHC\mathbf{H}_2$), 2.55 (t, J_{HH} 6.3 Hz, $HN(CH_2)_2C\mathbf{H}_2NH_2$), 1.50 (qnt, $HNCH_2C\mathbf{H}_2CH_2NH_2$), 1.40 (br s, NH and OH).

7b. Anal. Calcd for $C_{38}H_{36}ClNP_2Ru$: C, 63.10; H, 5.30; N, 1.94. Found: C, 63.20; H, 5.56; N, 2.21. FAB MS, *m/z*: 705 (100) M^+; 670 (30) $[M - Cl]^+$; 598 (10) $[M-PhCH_2NH_2]$. ^{31}P NMR: δ 33.0 (s). Selected ^1H NMR data: δ 7.87 (m, Ph) and 7.37 (m, Ph), 4.84 (6H, s and overlapping m, $C_5\mathbf{H}_5$ and $P_2C\mathbf{H}CH_2$), 3.58 (2H, s, $PhC\mathbf{H}_2NH$), 2.65 (2H, dt, J_{HH} 7.2 Hz, J_{PH} 11.7 Hz, $P_2CHC\mathbf{H}_2$), 1.56 (3H, br s, N**H** and O**H**).

Derivatization of Electrodes with 3e. The appropriate electrodes (ITO-coated glass or anodized Pt disks) were soaked in a solution of **3e** (10 mM) in chlorobenzene for 24−48 h under nitrogen. They were then rinsed thoroughly with CH_2Cl_2, dried, and stored under dust-free conditions prior to cyclic voltammetry experiments.

Structure Determination. Data were collected using a Rigaku AFC6S diffractometer. Cell dimensions and intensities were determined using $\omega/2\theta$ scans. Structures were solved by direct methods,[29,30] and

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(29) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

Table 1. Crystallographic Data for **3b**·4MeOH

empirical formula $C_{62}H_{80}Cl_2N_4O_4P_4Ru$	fw 1241.21
$a = 11.448(6)$ Å	space group $P\bar{1}$ (No. 2)
$b = 13.10(1)$ Å	$T = 25$ °C
$c = 11.178(7)$ Å	$\lambda = 0.710\,69$ Å
$\alpha = 93.16(6)°$	$\rho_{calcd} = 1.250$ g cm^{-3}
$\beta = 99.51(5)°$	μ(Mo Kα) = 4.53 cm^{-1}
$\gamma = 92.29(5)°$	$R^a = 0.063$
$V = 1648(2)$ Å^3	$R_w{}^b = 0.070$
$Z = 1$	

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

Table 2. Significant Bond Lengths (Å) and Angles (deg) for **3b**

Bond Distances			
Ru(1)−Cl(1)	2.432(4)	P(2)−C(13)	1.83(1)
Ru(1)−P(1)	2.349(4)	P(2)−C(19)	1.85(1)
Ru(1)−P(2)	2.365(4)	P(2)−C(25)	1.86(1)
P(1)−C(5)	1.82(1)	C(25)−C(26)	1.49(2)
P(1)−C(10)	1.82(2)	C(26)−N(1)	1.47(2)
P(1)−C(25)	1.85(1)	N(1)−C(27)	1.45(2)
Bond Angles			
Cl(1)−Ru(1)−P(1)	95.5(1)	Ru(1)−P(2)−C(19)	127.9(5)
Cl(1)−Ru(1)−P(2)	98.9(1)	Ru(1)−P(2)−C(25)	94.1(5)
P(1)−Ru(1)−P(2)	71.5(1)	C(13)−P(2)−C(19)	100.3(6)
Ru(1)−P(1)−C(5)	123.1(5)	C(13)−P(2)−C(25)	109.4(7)
Ru(1)−P(1)−C(10)	123.7(5)	C(19)−P(2)−C(25)	105.0(6)
Ru(1)−P(1)−C(25)	94.8(5)	P(1)−C(25)−P(2)	95.8(6)
C(5)−P(1)−C(10)	100.2(7)	P(1)−C(25)−C(26)	120(1)
C(5)−P(1)−C(25)	107.0(6)	P(2)−C(25)−C(26)	124(1)
Ru(1)−P(2)−C(13)	118.4(5)	N(1)−C(26)−C(25)	112(1)

successive difference Fourier syntheses were used to locate all non-hydrogen atoms, followed by final refinements using full-matrix least-squares procedures. The TEXSAN crystallographic software package,[31] running on a microVAX computer, was used for computation of the structure, and ORTEP[32] was used to plot the molecular diagrams. Scattering factors and corrections for anomalous dispersion[33] were taken from standard references.[34] Experimental parameters and crystal data are given in Table 1, and selected bond lengths and angles are listed in Table 2. Full listings of H atom coordinates, bond distances and angles, and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

3b·4MeOH. Orange crystals of **3b** suitable for X-ray diffraction were obtained on layering a solution in toluene and excess 1,3-diaminopropane with MeOH. A crystal (0.10 × 0.10 × 0.25 mm) was mounted on a fiber and used for measurements of precise cell constants and collection of intensity data. Of 4298 unique reflections scanned in the range $2 < \theta < 25°$, 1913 with $F > 3.0\sigma(F)$ were used for structure solution and refinement. During data collection, three standard reflections, measured after every 150 reflections, declined by 1.01%. A linear correction factor was therefore applied to the data. Diffraction intensities were corrected for Lorentz and polarization effects.

Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding atom. Refinement converged at $R = 0.063$ ($R_w = 0.070$). The final electron density difference synthesis showed no peaks >0.51 or <-0.42 e Å^{-3}. The two MeOH solvate molecules in each asymmetric unit were distributed over three sites, and refinement was completed with 66.67% occupancy for each site.

Results and Discussion

Synthesis and Oxidation of *trans*-[RuCl$_2$(dppen)$_2$] (1). Treatment of [RuCl$_2$(PPh$_3$)$_3$] in CH_2Cl_2 with 2 mol equiv of dppen gave orange crystals of *trans*-[RuCl$_2$(dppen)$_2$]·CH_2Cl_2 (**1**) in over 85% yield. Complex **1** is sparingly soluble in toluene and is more soluble in chlorinated solvents. It is insoluble in acetone, acetonitrile, dmf, diethyl ether, and ethanol. It was reported previously as a serendipitous product of the reaction of [Ru$_2$(O$_2$CCH$_3$)$_4$Cl] with dppen in the presence of LiCl, and its crystal structure was determined.[35] Oxidation of **1** in CH_2Cl_2 with $NOBF_4$ gave dark green [RuCl$_2$(dppen)$_2$]BF$_4$ (**1**$^+$). This had satisfactory microanalyses, an FAB mass spectrum similar to that of **1**, and an IR spectrum similar to that of **1** except for an additional very strong band at 1055 cm^{-1} due to the BF_4^- anion. The electronic spectrum of **1**$^+$ in CH_2Cl_2 is very similar to that of *trans*-[RuCl$_2$(dppm)$_2$]BF$_4$.[22] This, and the IR spectrum, suggests that the *trans* geometry is retained on oxidation. Complex **1**$^+$ reverts to **1**, slowly in the solid state but much more rapidly in solution, making reliable extinction coefficients impossible to determine.

Synthesis of Amine Adducts of 1: 3a−g. We wished to examine the reactivity of **1** toward different nucleophiles in order to assess its utility in preparing metal−diphosphine complexes suitable for oxide surface derivatization. First, we explored reactions of **1** with primary amines. When **1** was suspended in toluene, or partially dissolved in chlorobenzene, and treated with a large (≥50-fold) excess of primary amine at room temperature, the color paled from orange to yellow and complete dissolution occurred over a period ranging from minutes to 16 h. The yellow solids isolated after workup were the hoped-for adducts *trans*-[RuCl$_2$({Ph$_2$P}$_2$CHCH$_2$NHR)$_2$] (R = PhCH$_2$, **3a**; R = (CH$_2$)$_3$NH$_2$, **3b**; R = *n*-octyl, **3c**; R = *R*-α-CH(Me)Ph, **3d**; R = (CH$_2$)$_3$Si(OEt)$_3$, **3e**). The adducts **3a**−**e** were soluble in CH_2Cl_2, $CHCl_3$, and chlorobenzene (a particularly useful solvent because it does not react with amines), sparingly soluble in aromatic solvents, but insoluble in polar aprotic solvents such as CH_3CN. The more polar **3b** was sparingly soluble in EtOH.

Secondary amines did not add so readily to **1**. Pyrrolidine added at room temperature under essentially the same conditions as for the primary amines, to give *trans*-[RuCl$_2$({Ph$_2$P}$_2$CHCH$_2$NC$_4$H$_8$)$_2$], **3f**. However, the addition of morpholine to **1a** to give **3g** required refluxing in toluene for 30 min. The adduct was not analytically satisfactory, although it displayed the expected M$^+$, [M − Cl]$^+$, and [M − Cl − HCl]$^+$ clusters in its FAB mass spectrum and had a singlet in its ^{31}P{^{1}H} NMR spectrum (below). The ^{1}H NMR spectrum of **3g** showed the presence of free morpholine in the sample, which could not be removed by recrystallization or vacuum-drying.

With diethylamine in chlorobenzene at room temperature, no reaction with **1** occurred, and on prolonged reflux, only a 20:80 mixture of *trans*- and *cis*-[RuCl$_2$(dppen)$_2$] was obtained; no addition to the dppen double bonds occurred. The same result was obtained with the less volatile amine HN(CH$_2$CH$_2$OCH$_3$)$_2$. It is notable that secondary amines also underwent more sluggish addition to [M(CO)$_4$(dppen)] (M = Cr, Mo, W) than did primary amines.[36] It is possible that steric factors are important here, since the bulky primary amine (CH$_3$)$_3$CCH$_2$NH$_2$ also failed to add to **1**.

We then tried adding secondary amines to **1**$^+$ in the hope that the more polarizing Ru(III) center would increase the reactivity of coordinated dppen toward nucleophiles; it is known that the Pt(IV) complex [PtIMe$_3$(dppen)] is significantly more

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(30) Beurskens, P. T. *DIRDIF: Direct Methods for Difference Structures—an automatic procedure for phase extension and refinement of difference structure factors*; Crystallography Laboratory: Toernooiveld, The Netherlands, 1984.

(31) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985.

(32) Johnson, C. K. ORTEPII; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(33) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(34) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(35) Cotton, F. A.; Diebold, M. P.; Matusz, M. *Polyhedron* **1987**, *6*, 1131.

(36) Cooper, G. R.; Hassan, F.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1985**, 614.

reactive than [$PtMe_2$(dppen)].[16] However, treatment of $\mathbf{1}^+$ with primary or secondary amines gave exclusively Ru(II) products with no apparent difference in reactivity.

The robust six-coordinate Ru(II) complexes **3a**−**g** are potentially suitable for further functionalization. In preliminary experiments, we have found that **3b** reacts with *p*-toluenesulfonyl chloride in CH_2Cl_2 to afford the corresponding insoluble tetrasulfonamide derivative (characterized by microanalyses, infrared spectroscopy, and FAB MS only). With salicylaldehyde, the primary amine groups of **3b** react to afford the corresponding bis(imine), which is also too insoluble for NMR spectroscopy. In principle, this opens the way to incorporation of **3b** in polymers (*via* condensation reactions) and supramolecular multimetallic redox centers (utilizing the salicylideamine groups as metal receptors), although such studies may be hampered by the limited solubility of the derivatives. There is also much current interest in polymeric siloxanes incorporating redox-active complexes,[28] and **3e** would be ideal for incorporation in such materials.

Spectroscopic Characterization of Complexes 1 and 3a−g. Fast atom bombardment mass spectrometry (FAB MS) of complexes **1** and **3a**−**g** revealed molecular ions as the base peaks, together with $[M - Cl]^+$ and, usually, $[M - Cl - HCl]^+$ clusters (see Experimental Section). The $^{31}P\{^1H\}$ NMR spectrum of **1** showed a singlet, at $\delta = +14.7$ ppm, consistent with *trans* geometry. The $^{31}P\{^1H\}$ NMR spectra of **3a**−**g** also showed singlets (except **3d**), shifted slightly upfield from the value for **1**. The $^{31}P\{^1H\}$ NMR spectrum of **3d** showed a triplet pattern centered at $\delta = 9.14$ ppm, with a separation of 35 Hz between the outer lines; this is because the two phosphorus nuclei in each ligand are rendered slightly inequivalent by the chiral amine substituent.

The ^1H NMR spectrum of **1** showed aromatic resonances at 7.5−7.1 ppm and a singlet due to the CH_2Cl_2 solvate. The $C{=}CH_2$ protons resonate as a pseudoquintet (apparent J_{PH} 12.6 Hz) at $\delta = 6.18$ ppm. This is a “virtual” quintet[37] and arises as a result of the strong P−*trans*-P coupling (300−350 Hz) typically observed for Ru(II)−phosphine complexes.[38,39] The four $C{=}CH_2$ protons and the four phosphorus nuclei formally comprise an AA′A″A‴XX′X″X‴ spin system. On the addition of nucleophiles to give **3a**−**g**, this resonance is replaced by multiplets at *ca.* $\delta = 5.4$ (1H) and 3.0 ppm (2H) for the P_2CHCH_2 moiety, with both types of proton coupled to each other and to the phosphorus nuclei (“virtual” coupling), in addition to resonances characteristic of the amine fragment. The appearance of these spectra is exemplified by that of **3b**, shown in Figure 1. Like the Pd(II) complexes studied earlier,[17] the adducts crystallize with significant amounts of solvent or water of crystallization, which cannot readily be removed by drying *in vacuo*. This is also evident in the ^1H NMR spectra.

Crystal Structure of 3b. Crystals of **3b** suitable for X-ray structure determination were obtained from CH_2Cl_2/MeOH by diffusion. The molecular structure is shown in Figure 2; significant bond lengths and angles are given in Table 2. As also found for the analogous complexes *trans*-[$RuCl_2(dppm)_2$],[40] *trans*-[$RuCl_2(Me_2C\{PPh_2\}_2)_2$],[41] and **1**,[35] there is a crystallographically-imposed center of symmetry at Ru for **3b**. It is possible that this particular stereoisomer is thermodynamically favored for these adducts for steric reasons. We have since obtained the crystal structure of an alcohol adduct of **1**, *trans*-[$RuCl_2\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}_2$], and this is similarly centrosymmetric.[42] It should be noted that **3b** crystallized as **3b**·4MeOH with the MeOH molecules distributed over three sites per asymmetric unit in the crystal lattice, and refinement was completed with 66.67% occupancy of each site, which probably accounts for the rather high R_w. In spite of the presence of these solvate molecules, no evidence was found for significant hydrogen bonding between the amine groups in **3b** and the solvate molecules.

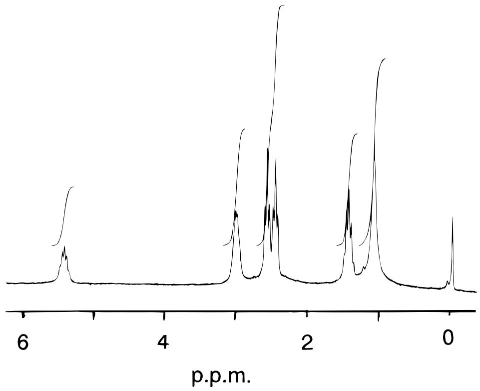

Figure 1. ^1H NMR spectrum (0−6 ppm region) of **3b** ($CDCl_3$, 400 MHz). Peaks (from low field): $P_2C\mathbf{H}CH_2$ (m), $P_2CHC\mathbf{H_2}$ (m), $CH_2NHC\mathbf{H_2}$ (t), $C\mathbf{H_2}NH_2$ (t), $CH_2C\mathbf{H_2}CH_2$ (quintet), $N\mathbf{H}/N\mathbf{H_2}$ (br s).

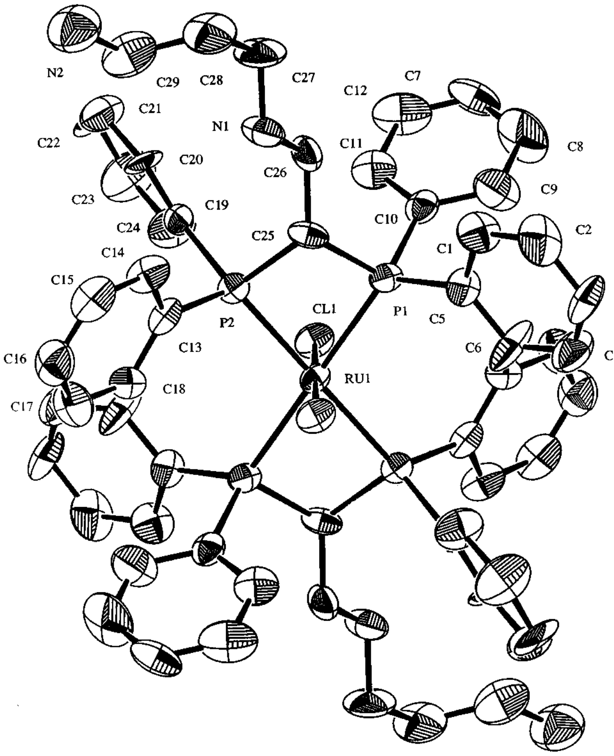

Figure 2. Molecular structure of **3b**.

In **1**, the $P-C({=}CH_2)-P$ angle is 98.6(1)°,[35] compared with 118.96(6)° for uncomplexed dppen,[43] a difference of 20.4°. In **3b**, the $P-CH(CH_2R)-P$ angle is 95.8(6)°. Although a free ligand closely analogous to the diphosphine unit in **3b** (for instance, $HMeC(PPh_2)_2$) has yet to be structurally characterized, it is unlikely that the P−C−P angle in such a ligand would be

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(37) Günther, H. *NMR Spectroscopy: Basic Principles, Concepts, and Applications in Chemistry*, 2nd ed.; Wiley: Chichester, U.K., 1995.

(38) Whinnery, L. L.; Yue, H. J.; Marsella, J. A. *Inorg. Chem.* **1986**, *25*, 4136.

(39) Lindner, E.; Möckel, A.; Mayer, H. A.; Kühbauch, H.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1993**, *32*, 1266.

(40) Chakravarty, A. R.; Cotton, F. A.; Schwotzer, W. *Inorg. Chim. Acta* **1984**, *84*, 179.

(41) Barkley, J. V.; Grimshaw, J. C.; Higgins, S. J.; Hoare, P. B.; McCart, M. K.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1995**, 2901.

(42) Higgins, S. J.; McCart, M. K.; Pounds, T. Unpublished work.

(43) Schmidbauer, H.; Herr, R.; Riede, J. *Chem. Ber.* **1984**, *117*, 2322.

larger than that found in free dppm, namely 106.16(5)°.[44] Therefore the angle strain has been reduced from 20.4° for **1** to, at most, 10.4° for **3b** as a consequence of nucleophilic addition to dppen. The reduction in angle strain is the likely driving force for the reaction. Both the metal−ligand distances and the bond lengths and angles in the four-membered chelate rings in **2b** are very similar to those in *trans*-[$RuCl_2$(dppm)$_2$].[40]

Reactions of 1 with Carbanions. The reactivity of **1** toward amine nucleophiles clearly mirrors that of the isoelectronic [$M(CO)_4$(dppen)] (M = Cr, Mo, W). The latter are known to react with carbanions,[13] and we therefore investigated the reaction of **1** with these nucleophiles. On treatment of an orange suspension of **1** in THF with a 6-fold molar excess of $LiC{\equiv}C(CH_2)_3CH_3$ in hexanes/Et_2O at *ca.* −20 °C, the mixture paled to almost colorless, and all the complex dissolved. Removal of solvent and trituration with cold MeOH afforded a tan solid **5**. The $^{31}P\{^1H\}$ NMR spectrum of **5** showed a singlet at +17.2 ppm, unusually somewhat downfield of the resonance for **1**. Microanalytical and FAB mass spectral data were consistent with the formula *trans*-[$Ru(C{\equiv}CR)_2(\{Ph_2P\}_2CHCH_2C{\equiv}CR)_2$] (R = ^nBu) for **5**. In particular, the FAB mass spectrum showed a weak cluster of peaks due to M^+ and stronger peaks corresponding to progressive loss of $HC{\equiv}C^nBu$ fragments. No peaks due to loss of chloride ions could be discerned. Moreover, an analytical test for chloride proved negative. The ^1H NMR spectrum showed resonances characteristic of the ligand P_2CHCH_2- moiety (unusually, coupling between the $P_2CHC\mathbf{H}_2$ protons and the phosphorus nuclei was too weak to be observed in this complex) and distinct resonances for the two ($Ru-C{\equiv}CR$ and $P_2CHCH_2C{\equiv}CR$) sets of *n*-butyl environments; we do not know which is which. We also obtained an off-white solid on treatment of **1** with $LiC{\equiv}CPh$, but the insolubility of this product has hindered characterization. The FAB mass spectrum showed clusters of peaks at M^+ and $[M - HC{\equiv}CPh]^+$, consistent with the formulation [$Ru(C{\equiv}CPh)_2(\{Ph_2P\}_2CHCH_2C{\equiv}CPh)_2$], but also showed weak peaks at higher mass.

There is considerable current interest in metal−acetylide conjugated polymers, including $\{[Ru(diphos)_2(-C{\equiv}C-R-C{\equiv}C-)]\}_n$ (diphos = dppe, $Et_2PCH_2CH_2PEt_2$), but these are normally made from the chlorides using organotin acetylides;[45] lithium acetylides have not commonly been used to prepare Ru(II)−acetylide complexes. Attempts to react **1** with acetylenes ($Bu^nC{\equiv}CH$, propargyl alcohol) and tertiary amine bases [NEt_3 or 1,8-bis(dimethylamino)naphthalene] in the presence of CuI failed to yield acetylide complexes, although similar reactions have been employed successfully using *cis*-[$RuCl_2$(dppm)$_2$].[46] The more electron-rich complexes *trans*-[$RuCl_2(L-L)_2$] (L−L = $R_2PCH_2CH_2PR_2$; R = Me, Et) are reported to react with terminal acetylenes $R'C{\equiv}CH$ in alcohol in the presence of sodium alkoxide to give *trans*-[$Ru(C{\equiv}CR')_2(L-L)_2$],[47] but **1** did not react under these conditions.

Interestingly, other nucleophilic carbanions did not react with **1**. For example, **1** was recovered in high yield from reactions with sodium diethylmalonate or sodium acetylacetonate in chlorobenzene/butanol and from attempts to react **1** with $H_2C(CO_2Et)$ in chlorinated solvents in the presence of 1,8-bis(dimethylamino)naphthalene. This was unexpected, since sodium diethylmalonate in dry thf adds readily to [$M(CO)_4$(dppen)] (M = Mo, W).[13]

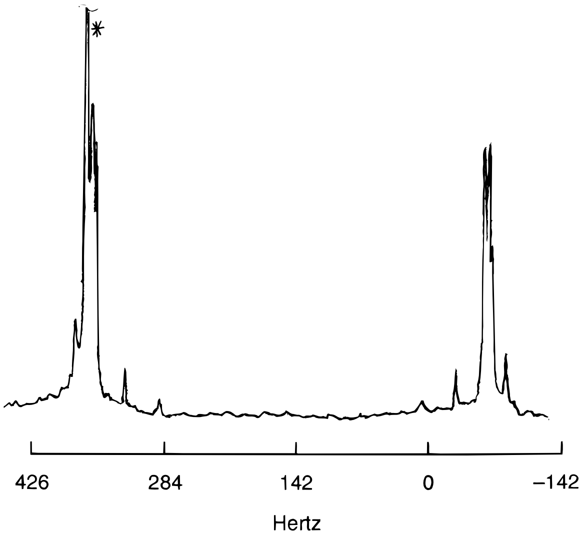

Figure 3. ^{31}P NMR spectrum of **2** ($CDCl_3$, 24.3 MHz, line width *ca.* 3 Hz). The starred peak is due to an impurity of **1** in this sample.

Synthesis and Chemistry of *cis*-[$RuCl_2$(dppen)$_2$] (2) and Amine Adducts 4a,b. On reflux in chlorobenzene for 16 h, with changes being monitored by $^{31}P\{^1H\}$ NMR spectroscopy, **1** gave a 10:90 mixture of **1** and another complex, which still analyzed satisfactorily for [$RuCl_2$(dppen)$_2$]. The latter is *cis*-[$RuCl_2$(dppen)$_2$] (**2**). That this 10:90 mixture of **1** and **2** is the thermodynamic product is strongly suggested by the fact that prolonged (>48 h) reflux in chlorobenzene (bp 132 °C) or 1,2-dichlorobenzene (bp 180 °C) resulted in no further change. Pure **2** was obtained by extracting the crude product with MeOH (in which **2** is sparingly soluble) as a pale yellow solid. In $CDCl_3$, on exposure to laboratory light, **2** reverts completely to **1** over a period of a few days. The complex was therefore handled and stored in the dark. Similar thermal conversion of *trans*-[$RuCl_2$(dppm)$_2$] (dppm = $Ph_2PCH_2PPh_2$) to *cis*-[$RuCl_2$(dppm)$_2$] (16 h reflux in 1,2−dichloroethane), and photochemical conversion of *cis*-[$RuCl_2$(dppm)$_2$] to *trans*-[$RuCl_2$(dppm)$_2$] in solution, has been reported.[21]

The addition of amines to **2** was more sluggish than the addition to **1**, and steric requirements appear more stringent. Thus, adducts with (*n*-hexyl)NH_2 (**4a**) and with $(EtO)_3Si(CH_2)_3NH_2$ (**4b**) were successfully isolated. Interestingly, whereas **4a** was soluble in chlorinated solvents, **4b** was almost totally insoluble, once isolated by hexane precipitation from solution in chlorobenzene/excess amine during its synthesis, and accordingly the $^{31}P\{^1H\}$ and ^1H NMR spectra for **4b** (Experimental Section) were obtained using $CDCl_3$ solutions of the crude oil remaining after pumping off chlorobenzene and most of the excess amine. The ^1H NMR spectrum showed resonances due to **4b** as detailed in the Experimental Section, together with resonances due to residual $(EtO)_3Si(CH_2)_3NH_2$.

NMR Spectroscopic Characterization of 2 and 4a,b. The $^{31}P\{^1H\}$ NMR spectrum of **2** at 101.2 MHz showed two apparent singlets of equal intensity at −3.56 and 13.85 ppm, which we assign to P−*trans*-Cl and P−*trans*-P respectively, since the latter resonance is close to that of **1**. A spectrum recorded at 24.3 MHz (JEOL FX60; *ca.* 3 Hz line width; Figure 3) revealed these to be, in fact, second-order multiplets, consistent with the expected AA′XX′ spin system. The program gNMR (Version 3.6r5, IvorySoft; Apple Macintosh Performa 6320) was used to model this behavior. The peak positions and relative intensities could be approximately simulated by employing the following values for the coupling constants of

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[44] Schmidbauer, H.; Reber, G.; Schier, A.; Wagner, F. E.; Muller, G. *Inorg. Chim. Acta* **1988**, *147*, 1988.

[45] Atherton, Z.; Faulkner, C. W.; Ingham, S. L.; Kakkar, A. K.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1993**, *462*, 265.

[46] Pirio, N.; Touchard, D.; Dixneuf, P. H.; Fettouli, M.; Ouahab, L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 651.

[47] Field, L. D.; George, A. V.; Hockless, D. C. R.; Purches, G. R.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1996**, 2011.

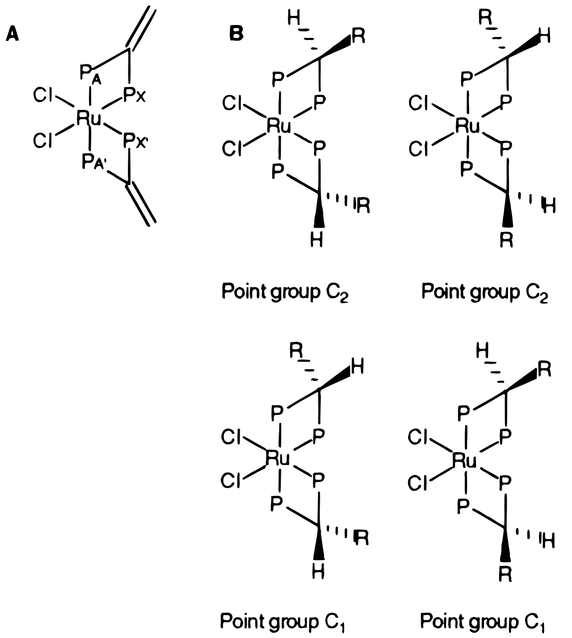

Figure 4. (A) Labeling used in the discussion of the spin system for the ^{31}P NMR spectrum of **2**. (B) Possible isomers of amine adducts of **2**. Since the point group of these is C_2 or C_1, each has a nonsuperimposable mirror image, giving eight possible diastereoisomers in total.

the AA′XX′ spin system appropriate for the ^{31}P{^{1}H} NMR spectrum of *cis*-[RuCl$_2$(dppen)$_2$]) (Figure 4A): $J_{AA'}$ +405 Hz, J_{AX} +40 Hz, $J_{AX'}$ −44 Hz, and $J_{XX'}$ −30 Hz. The absolute values of these coupling constants are reasonable for octahedral Ru(II).[38,48] For the signals at 101.2 MHz to appear as singlets, it is clear that J_{AX} ($=J_{A'X'}$) must be similar in magnitude, but opposite in sign, to $J_{AX'}$ ($=J_{A'X}$) and $J_{XX'}$. Whereas P−*cis*-P coupling constants are negative if the coupling is exclusively "through-the-metal"[49] (typically *ca.* −35 Hz for Ru(II)[50]), in chelate ligands the observed P−P coupling is the algebraic sum of "through-the-metal" and "through-the-backbone" contributions. The "through-the-backbone" contribution is usually positive for ligands containing a one-carbon bridge and can be particularly large for dppen (*ca.* 100 Hz in Cr(0)−, Mo(0)−, and W(0)−carbonyl complexes).[49] The "through-the-backbone" contribution in this complex is therefore *ca.* +84 Hz. This results in a net positive P−*cis*-P coupling constant when the P nuclei are connected by a C═CH$_2$ backbone.

The C═CH$_2$ resonance in the ^{1}H NMR spectrum of **2** is, as expected, a complex symmetrical multiplet, centered at 6.02 ppm, partially overlapping the residual signal due to **1**. Interestingly, whereas the phenyl protons in the spectrum of **1** resonate as closely-spaced overlapping multiplets from 7.5 to 7.1 ppm, the phenyl protons of **2** resonate as a series of distinct multiplets between 8.25 and 6.52 ppm, presumably because steric crowding in the *cis* complex causes some of these protons to be in unusual environments.

The ^{31}P{^{1}H} NMR spectra of **4a** and **4b** showed two triplets, at *ca.* 27 and 12 ppm, with $|J_{AX} + J_{AX'}| = 58$ Hz. Interestingly, these are shifted considerably *down*field (by *ca.* 15 ppm) from the apparent singlets seen for **2**, whereas the resonances for **3a**−**e** were shifted *up*field slightly from that due to **1**. Also notable is the reversion to the normal AA′XX′ "virtual" triplets as the ligand backbone changes from P$_2$C═CH$_2$ to P$_2$CHR.

The ^{1}H NMR spectra of **4a** and **4b** are more complicated than those of **3a**−**e**, and the resonances due to the P$_2$C**H**C**H**$_2$-NHR moiety appear as broad singlets; individual coupling to phosphorus and to neighboring protons were not resolved. The resonances due to the P$_2$CHC**H**$_2$NHR methylene, in particular, are at significantly higher field than those of the corresponding protons in **3a**−**e**. It is likely that **4a** and **4b** are mixtures of at least some of the eight possible diastereomers (Figure 4B), and this could be responsible for the broad proton signals. We have not yet been able to isolate X-ray-quality single crystals of **4a**.

It did not prove possible to isolate adducts of **2** with secondary amines, PhCH$_2$NH$_2$ or *R*-α-H$_2$NCH(Me)Ph, although partial addition did occur as revealed by ^{31}P{^{1}H} NMR spectroscopy; two downfield triplets were seen in the ^{31}P{^{1}H} NMR spectra of mixtures of **2** and excess PhCH$_2$NH$_2$, and four triplets (partially overlapping) were seen in the ^{31}P{^{1}H} NMR spectra of mixtures of **2** and excess *R*-α-PhCH(Me)NH$_2$.

Electronic Spectra of 1, 2, and 3b. The complexes [RuX$_2$-(diphosphine)$_2$] range in color from pale yellow to orange. The electronic spectra of *trans*-[RuX$_2$(diphosphine)$_2$] usually show two d−d bands in the visible region, a lower energy band assigned as $^1A_{1g} \rightarrow {}^1E_g$ and a higher energy band assigned as $^1A_{1g} \rightarrow {}^1A_{2g}$, assuming approximate D_{4h} symmetry.[51] *cis*-[RuX$_2$-(diphosphine)$_2$] complexes usually have d−d bands at somewhat higher energy, which accounts for their generally paler color.[21,51] The spectrum of orange **1** in CH$_2$Cl$_2$ shows a single, rather broad and surprisingly intense (ϵ = 2240 L mol^{-1} cm^{-1}) band at 24 150 cm^{-1}. The electronic spectrum of a representative amine adduct, **3b**, in CH$_2$Cl$_2$, showed two much weaker d−d bands, at 20 580 and 23 920 cm^{-1} (ϵ = 110 and 210 L mol^{-1} cm^{-1}, respectively), assigned to the $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions; this spectrum is very similar to that of *trans*-[RuCl$_2$-(dppm)$_2$].[21] The decrease in extinction coefficient on amine addition is reflected in the colors of the amine adducts, which are all paler than **1**. The electronic spectrum of **2** in CH$_2$Cl$_2$ shows d−d bands at 22 730 (shoulder) and 27 170 cm^{-1}, at higher energy than those for **1**, but reliable extinction coefficients could not be obtained since solutions of **2** invariably contain some **1**, as shown by ^{31}P{^{1}H} NMR spectroscopy and cyclic voltammetry (below).

Solution Electrochemistry of Complexes 1−3e. In cyclic voltammetry experiments in CH$_2$Cl$_2$, **1** and **3a**−**e** showed reversible Ru(II)/Ru(III) couples at *ca.* +0.01 V (±0.03 V; Experimental Section), similar to those found earlier for a series of *trans*-[RuCl$_2$(L−L)$_2$] complexes.[22] Since such major variation as altering the donor atom or chelate ring size for the neutral ligands has little effect on Ru(II)/Ru(III) potentials for this family of complexes, it is not surprising that the addition of nucleophiles to **1** has almost no effect on the Ru(II)/Ru(III) potential. The voltammetry of **3a**−**e** was complicated by the precipitation of material from solution. Infrared evidence suggested that quaternization of the amine group(s) by solvent had occurred. The precipitates were too insoluble for NMR characterization.

The cyclic voltammogram of **2** was investigated both in CH$_3$-CN/0.2 M tetraethylammonium tetrafluoroborate (TEAT), in which it was sparingly soluble, and in CH$_2$Cl$_2$/0.2 M TBAT. In CH$_3$CN, a broad oxidation process, centered at +0.52 V, an associated broad reduction wave at +0.37 V, and an oxidation at +0.90 V were observed. The voltammogram is similar to that observed earlier for *cis*-[RuCl$_2$(dppm)$_2$] in a CH$_3$CN/CH$_2$-Cl$_2$ mixture.[21] The redox waves were assigned respectively to the formation and re-reduction of chlorine from chloride ions present as a result of solvolysis of *cis*-[RuCl$_2$(dppm)$_2$] to

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(48) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635.

(49) Bookham, J. L.; Fontaine, X. L. R.; Kennedy, J. D.; McFarlane, W. *Inorg. Chem.* **1988**, *27*, 1111.

(50) Baker, M. V.; Field, L. D. *Inorg. Chem.* **1987**, *26*, 2010.

(51) Klassen, D. M.; Crosby, G. A. *J. Mol. Spectrosc.* **1968**, *25*, 398.

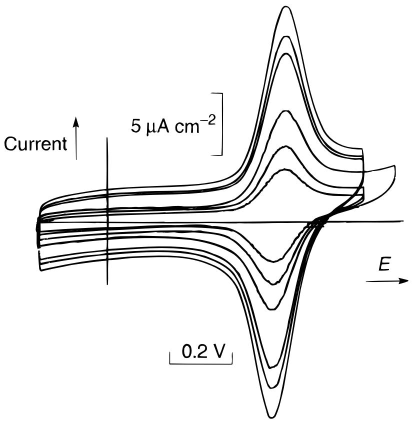

Figure 5. CV's of a monolayer of **3e** on an ITO electrode, recorded in CH_3CN/0.2 M TEAT. Sweep rates (with increasing peak currents) were respectively 50, 75, 100, 150, 200, and 250 mV s^{-1}. Peak currents were linear with scan rate up to *ca.* 150 mV s^{-1}.

$[RuCl(CH_3CN)(dppm)_2]Cl$ and to the Ru(II)/Ru(III) wave for the cationic Ru(II) complex. Clearly, an analogous solvolysis is occurring for *cis*-$[RuCl_2(dppen)_2]$. The only difference is that whereas the Ru(II)/Ru(III) wave was reversible in CH_3CN/CH_2Cl_2 for the dppm complex, it is totally irreversible for $[RuCl(CH_3CN)(dppen)_2]^+$ in CH_3CN. The rather positive oxidation potential, compared with that for **1**, for example, arises because cationic Ru(II) complexes are harder to oxidize than neutral species and because the metal center has lost a π-donor halide ligand which would stabilize the Ru(III) state.

The $^{31}P\{^1H\}$ NMR spectrum of a saturated solution of **2** in CH_3CN showed the formation of a single species, with complex multiplets centered at −0.95, 13.60, and 20.70 ppm, in approximately a 2:1:1 intensity ratio. This suggests an AA′MX spin system, consistent with a *cis*-$[RuCl(CH_3CN)(dppen)_2]^+$ moiety. *Cis* stereochemistry had earlier been assumed for the complex $[RuCl(CH_3CN)(dppm)_2]Cl$[21] without supporting spectroscopic evidence.

In CH_2Cl_2, a very different voltammogram was observed. Upon a positive scan from −0.4 V, a weak, reversible wave at +0.01 V, due to the presence of traces of **1**, was seen, together with a much stronger redox wave centered at +0.41 V, which we assign to the **2**/**2**$^+$ couple; for *cis*-$[RuCl_2(dppm)_2]$, the Ru(II)/Ru(III) couple was similarly 0.37 V positive of the potential for the *trans* isomer.[21] The reversibility of the **2**/**2**$^+$ couple did not vary appreciably as a function of scan rate (5−200 mV s^{-1}). Moreover, the small peaks due to the **1**/**1**$^+$ couple did not increase in intensity on repetitive scanning through the **2**/**2**$^+$ couple. This suggests that *cis*-$[RuCl_2(dppen)_2]^+$ is stable on the voltammetric time scale, unlike *cis*-$[RuCl_2(dppm)_2]^+$, which was shown to undergo isomerization to *trans*-$[RuCl_2(dppm)_2]^+$.[21]

Functionalization of Electrodes with 3e. Clean ITO-coated glass was soaked in a chlorobenzene solution (10 mM) of **3e**. After thorough washing with dichloromethane and acetone, these electrodes were examined by cyclic voltammetry in 0.2 M TEAT in CH_3CN, from *ca.* −0.7 to +0.3 V. A typical example is shown in Figure 5. Although for an ideal surface-localized redox process the cathodic and anodic current peaks should occur at the same potential,[9] and indeed this has been observed for functionalized Pt electrodes,[52] there is a peak-to-peak separation of 40 mV in our experiment. However, this remains invariant with scan rate up to 250 mV s^{-1} (Supporting Information). Moreover, larger peak-to-peak separations have been observed in the voltammetry of ferrocenes surface-anchored to ITO in similar fashion.[45,53] The $E_{1/2}$ value, +0.03 V (*vs* ferrocene/ferrocenium), corresponds closely to those for **3a**−**d** in CH_2Cl_2 solution. As an indirect check that the anchoring did indeed involve reaction of the triethoxysilane groups in **3e** with the surface, we repeated the derivatization process using **1**, *trans*-$[RuCl_2(dppm)_2]$, and **3a**. No difference was observed between the voltammetry of these and untreated electrodes; the terminal triethoxysilyl groups are essential for successful derivatization.

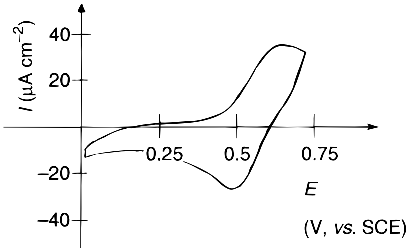

Figure 6. CV of a monolayer of **3e** on an anodized Pt electrode, recorded in CH_3CN/0.2 M TEAT.

The unit cell volume of **3b** is 1648(2) Å^3 ($Z = 1$). Since **3b** and **3e** are very similar, the area occupied on the surface by a molecule of **3e** can be approximated by the product of two of the unit cell dimensions of **3b**. An upper limit for this is therefore approximately 150 Å^2. A lower limit for the charge passed on oxidizing a monolayer of **3e** in a 1-electron process is therefore 10.7 μC cm^{-2}; this assumes a smooth electrode surface and close packing. The area under the anodic wave in voltammograms of ITO electrodes modified with **3e** was consistently 15 ± 3 μC cm^{-2}. This is consistent with an approximate monolayer coverage of the electrode by **3e**; the difference is accounted for by electrode roughness. Our modified electrodes therefore have much in common with earlier work using classical complexes such as Ru(II)−bipyridine derivatives.[3−5]

The modified electrodes are highly stable to prolonged cycling in acetonitrile. Although the anodic peak current for the electrode of Figure 5 declined by 7% over 100 scans between −0.7 and +0.3 V, it did not then significantly change after another 1000 scans. Interestingly, although these complexes are insoluble in water, the Ru(II)/Ru(III) redox process for electrodes modified with a monolayer of **3e** in aqueous buffer (0.1 M Na_2HPO_4/0.1 M NaCl) was seen at the same formal potential as in CH_3CN, and the redox peak currents did not appreciably decline over 100 scans in this medium.

Another approach often used to attach metal complexes to oxide electrode surfaces has been to derivatize the surface with an amine-terminated silyl anchor and then to couple the amine with some functionality (often a carboxylic acid) on the metal complex.[52] We therefore tried modifying ITO-coated glass slides with $(EtO)_3Si(CH_2)_3NH_2$ and then reacting these with **1** in chlorobenzene/NEt_3. Monolayer or sub-monolayer coverage of the anchored complex was sometimes observed by cyclic voltammetry, but more often the procedure failed. This is consistent with the fact that successful syntheses of **3a**−**e** (as monitored by $^{31}P\{^1H\}$ NMR spectroscopy in solution) required >10-fold excess of amine.

Platinum electrodes become coated with a hydrated platinum oxide layer on anodizing in aqueous H_2SO_4, and monolayers have been successfully deposited on such electrodes.[28,52] Therefore we attempted to anchor **3e** to anodized Pt electrodes similarly. Figure 6 shows a voltammogram for such an electrode. The charge under the anodic wave for a freshly-

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(52) Abruña, H.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1979**, *11*, 3233.

(53) Wilson, R.; Schiffrin, D. J. *Analyst (London)* **1995**, *120*, 175.

derivatized electrode typically corresponded to *ca*. 20 monolayers. This is too large to be accounted for by surface roughness[52] and suggests that polymerization of the siloxy groups of **3e** occurs during electrode modification, resulting in a polymer layer on the electrode. Peak currents did not vary linearly with scan rate for these electrodes, and the peak-to-peak separation increased with scan rate, probably owing to slow electron transfer kinetics. Also, the peak currents declined by 20−30% over 100 scans between −0.6 and +0.3 V, presumably owing to desorption of material from the electrode surface or to progressive insulation of some of the redox sites from the electrode surface. It is known that attempts to modify electrodes using this reaction in the presence of traces of water can lead to multilayers.[54] Moreover, even after oven drying, hydrous oxides can still retain water. Polymerization will be more likely with a substrate such as **3e**, bearing two pendant siloxy groups, than with molecules like $[(\{EtO\}_2MeSi\{CH_2\}_3NHCOC_5H_4)FeCp]$ used by other workers.[28]

Attempts to prepare ITO electrodes modified using the *cis* isomer **4b** were frustrated by its insolubility in any solvent compatible with electrochemistry. We therefore refluxed ITO electrodes coated with a monolayer of **3e** in chlorobenzene for up to 16 h, in attempts to isomerize the surface-anchored complex from *trans* to *cis*. Subsequent cyclic voltammetry of these electrodes in CH_2Cl_2/0.2 M TBAT revealed a small, broad redox wave at +0.03 V, probably due to residual surface-anchored **3e**, and a totally irreversible oxidation which commenced at +0.50 V and which disappeared on repeated scanning.

Amine Adducts of [CpRuCl(dppen)] (6). We have examined the addition of nucleophiles to the "half-sandwich" complex [CpRuCl(dppen)][23] (**6**). The anchoring of this more reactive organometallic center to electrode or oxide surfaces would be of interest. Moreover, with only a single pendant trialkoxysilyl group, it was anticipated that an adduct of **6** with $(EtO)_3Si(CH_2)_3NH_2$ would lessen the problems of multilayer formation.

With an excess of 1,3-diaminopropane or benzylamine in toluene, **6** reacted to give the adduct $[CpRuCl(\{Ph_2P\}_2CHCH_2NHR)]$ (R = $(CH_2)_3NH_2$ (**7a**) or CH_2Ph (**7b**), respectively); characterization data are given in the Experimental Section. It proved difficult to free these very soluble adducts from excess amine, and yields were low. With $H_2N(CH_2)_3Si(OEt)_3$, addition occurred (monitored by $^{31}P\{^1H\}$ NMR) but the adduct could not be isolated free of excess amine.

Conclusions

We have used the reactivity of coordinated dppen toward nucleophiles to construct the new ruthenium(II) complexes of amine-functionalized diphosphine ligands *trans*-$[RuCl_2\{(Ph_2P)_2CHCH_2NRR'\}_2]$, including an example suitable for surface-anchoring to oxide supports, **3e**; these could be electrode surfaces, as demonstrated here, or inert oxides as commonly used in the "heterogenizing" of homogeneous catalysts. These complexes also have potential for incorporation into polymers *via* condensation reactions (e.g., **3b**) or silica gels *via* controlled hydrolysis (**3e**). We have demonstrated the anchoring of a monolayer of **3e** to ITO electrodes using cyclic voltammetry of the surface-localized complex. Future work will probe the effects of changing the metal center and coligands upon this chemistry, and further exploration of the reactivity of **1** and **2** with alkynes is in hand.

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Supporting Information Available: A diagram showing the anodic peak current *vs* scan rate for Figure 5 (1 page). An X-ray crystallographic file, in CIF format, for complex **3b**·4MeOH is available on the Internet only. Ordering and access information is given on any current masthead page.

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(54) Lenhard, J. R.; Murray, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 7870.