JOM 23460

Facile route for the synthesis of triosmium and triruthenium isocyanide complexes

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(Received July 24, 1992; in revised form December 11, 1992)

Abstract

The osmium isocyanide complexes $Os_3(CO)_{11}(CNR)$ (**1a**, R = Pr; **1b**, R = ^{i}Pr; **1c**, R = CH_2Ph; **1d**, R = Ph) are synthesized in high yields by reaction of $Os_3(CO)_{12}$ with phosphine imides via a deoxygenation mechanism. These complexes react with an additional equivalent of $Ph_3P{=}NR$ to yield the diisocyanide complexes $Os_3(CO)_{10}(CNR)_2$ (**2a**, R = Pr; **2b**, R = ^{i}Pr; **2c**, R = CH_2Ph; **2d**, R = Ph). The reaction of $Os_3(CO)_{10}(CNCH_2Ph)_2$ with excess $Ph_3P{=}NPr$ or $Ph_3P{=}NCH_2Ph$ in refluxing benzene gives $Os_3(CO)_9(CNCH_2Ph)_2(CNR)$ (**3a**, R = Pr; **3b**, R = CH_2Ph). The ruthenium isocyanide derivatives $Ru_3(CO)_{11}(CNR)$ (**4a**, R = Pr; **4b**, R = ^{i}Pr, **4c**, R = CH_2Ph; **4d**, R = Ph) are also prepared by reaction of $Ru_3(CO)_{12}$ with phosphine imide. It was observed that geometrical and electronic characteristics of the imide play key roles in controlling the rate of the reaction.

1. Introduction

The general route for the synthesis of metal isocyanide complexes is via the substitution of the coordinated CO group in complex by an organo isocyanide ligand [1]. Mays *et al.* [2] prepared the osmium isocyanide clusters by this strategy. The Os–CO bond is relatively strong [3] and substitution reactions of dodecacarbonyltriosmium when effected by thermal or photochemical methods often lead to an assortment of products. Bruce *et al.* [4] subsequently followed a similar strategy, but they used catalytic amounts of Ph_2CO^-, to synthesize the isocyanide derivatives of the M_3 cluster (M = Fe, Ru, Os). Yields of the products, $Os_3(CO)_{11}(CNR)$, were not in these cases satisfactory. It was therefore thought worth seeking a more convenient and effective strategy to prepare these isocyanide complexes, and this led us to attempt an alternative route for their preparation by utilizing phosphine imide as a deoxygenating reagent.

Although many reactions have been reported between phosphine imides and organo-transition metal complexes [5], deoxygenation by phosphine imides of the metal carbonyl to form metal isocyanide complexes is rare [6]. Previously we reported studies on the deoxygenation of $ReBr(CO)_5$ by phosphine imide to afford the rhenium isocyanide complexes $ReBr(CO)_4(CNR)$ in very high yield [7]. Here we report the preparation of several osmium and ruthenium isocyanide clusters derived from the ylide-type reaction of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ with phosphine imides. Some aspects of this work have been communicated previously [8].

2. Results and discussion

2.1. Preparation of $Os_3(CO)_{11}(CNR)$ and $Os_3(CO)_{10}(CNR)_2$

$Os_3(CO)_{12}$ reacts with one equivalent of $Ph_3P{=}NR$ in CH_2Cl_2 at room temperature to give the osmium isocyanide complexes $Os_3(CO)_{11}(CNR)$ (**1a**, R = Pr; **1b**, R = ^{i}Pr, **1c**, R = CH_2Ph) in high yields. The complexes **1a** and **1c** can react further with an additional equivalent of the corresponding $Ph_3P{=}NR$ at room tempera-

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0022-328X/93/$6.00

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ture to afford the diisocyanide complexes $Os_3(CO)_{10}(CNR)_2$ (**2a**, R = Pr; **2c**, R = CH_2Ph) (eqn. (1)). Complexes **2a** and **2c** can also be obtained directly from reaction of $Os_3(CO)_{12}$ with two equivalents of $Ph_3P{=}NR$

$$Os_3(CO)_{12} \xrightarrow[\text{r.t.}]{Ph_3P=NR,\ CH_2Cl_2} \underset{\substack{\mathbf{1a},\ R=Pr,\ 92\% \\ \mathbf{1b},\ R={}^iPr,\ 88\% \\ \mathbf{1c},\ R=CH_2Ph,\ 90\%}}{Os_3(CO)_{11}(CNR)} + \underset{\substack{\mathbf{2a},\ R=Pr,\ 4\% \\ \mathbf{2b},\ R={}^iPr,\ 0\% \\ \mathbf{2c},\ R=CH_2Ph,\ 5\%}}{Os_3(CO)_{10}(CNR)_2} \quad (1)$$

$Ph_3P{=}NR$ (R = Pr, CH_2Ph) in CH_2Cl_2 at room temperature. The monoisocyanide complex **1** was verified to be the intermediate yielding **2** when this reaction was monitored by infrared spectroscopy. The IR spectrum shows that the ratio of the absorptions ν(CN) to ν(CO) is stronger in **2** than in **1**, indicating that the strength of the ν(CN) peak follows the trend of number of the coordinated isocyanide ligands in the cluster sphere. However, treatment of $Os_3(CO)_{12}$ with excess of $Ph_3P{=}N^iPr$ at room temperature gives only the monoisocyanide complex $Os_3(CO)_{11}(CN^iPr)$. More vigorous conditions (in refluxing CH_2Cl_2) are needed to afford the diisocyanide complex $Os_3(CO)_{10}(CN^iPr)_2$ (**2b**), indicating that the reactivity of $Ph_3P{=}N^iPr$ is weaker than that of $Ph_3P{=}NPr$ towards the Os cluster. $Ph_3P{=}NPh$, being a more weakly nucleophilic reagent than $Ph_3P{=}NPr$, reacts with $Os_3(CO)_{12}$ in refluxing benzene to form mainly the monoisocyanide complex $Os_3(CO)_{11}(CNPh)$ (**1d**) and the minor diisocyanide complex $Os_3(CO)_{10}(CNPh)_2$ (**2d**) (eqn. (2)).

$$Os_3(CO)_{12} \xrightarrow[\text{benzene, reflux}]{Ph_3P=NPh} \underset{\mathbf{1d},\ 74\%}{Os_3(CO)_{11}(CNPh)} + \underset{\mathbf{2d},\ 14\%}{Os_3(CO)_{10}(CNPh)_2} \quad (2)$$

2.2. Preparation of $Os_3(CO)_9(CNCH_2Ph)_2(CNR)$ (R = Pr, CH_2Ph)

An attempt to synthesize the multiisocyanide complexes $Os_3(CO)_{12-x}(CNPr)_x$ ($x \geq 3$) was made by treating $Os_3(CO)_{12}$ with excess $Ph_3P{=}NPr$ in refluxing toluene. Some decomposed complexes were obtained instead of the expected products $Os_3(CO)_9(CNPr)_3$, showing that $Os_3(CO)_{10}(CNPr)_2$ is reluctant to continue accepting nucleophilic attack by phosphine imides. In the case of $Os_3(CO)_{10}(CNCH_2Ph)_2$, it shows that deoxygenation by $Ph_3P{=}NPr$ or $Ph_3P{=}NCH_2Ph$ in refluxing benzene can take place to give $Os_3(CO)_9(CNCH_2Ph)_2(CNR)$ (**3a**, R = Pr; **3b**, R = CH_2Ph) (eqn. (3)). The new ligand $Ph_3{=}NCH_2Ph$, prepared following similar procedures [9], reacts readily with $Os_3(CO)_{12}$ at room temperature to form $Os_3(CO)_{11}(CNCH_2Ph)$ and $Os_3(CO)_{10}(CNCH_2Ph)_2$ [10]. Compared to the propyl group, the benzyl group in coordinated $CNCH_2Ph$, with its relatively stronger electron withdrawing ability, introduces a more positive charge on the carbonyl carbon, consequently making $Os_3(CO)_{10}(CNCH_2Ph)_2$ more susceptible to nucleophilic attack.

$$Os_3(CO)_{10}(CNCH_2Ph)_2 \xrightarrow[\text{benzene, reflux}]{Ph_3P=NR} \underset{\substack{\mathbf{3a},\ R=Pr,\ 25\% \\ \mathbf{3b},\ R=CH_2Ph,\ 19\%}}{Os_3(CO)_9(CNCH_2Ph)_2(CNR)} \quad (3)$$

The IR spectra in solution of all the monoisocyanide derivatives $Os_3(CO)_{11}(CNR)$ are essentially identical. The pattern of the ν(CO) bands is very different from that observed for the (equatorially) monosubstituted phosphine derivatives [11]. This evidence alone suggests that the isocyanide ligand is axially rather than equatorially substituted. Average ν(CN) decreases as the substitution of isocyanide increases, suggesting that relatively more charge is delocalized into the CNR π^* orbitals as the number of CO groups available for this purpose decreases [2a].

The ^{13}C NMR spectrum of $Os_3(CO)_{11}(CNPr)$ (**1a**) at $-50°C$ shows five carbonyl signals at δ 186.1, 184.3, 183.6, 173.4 and 171.9 with intensity ratio 2:2:1:4:2. This is consistent with the axially substituted structure as analyzed by Mays [2a]. On warming **1a**, a gradual broadening of resonances is observed, and the spectrum shows three broad peaks at δ 183.2, 173.3 and 172.0 at room temperature. This indicates that **1a** in solution is fluxional on the NMR time scale at ambient temperature and only the axial isomer is present in significant concentrations at low temperature. The ^{13}C NMR spectrum of $Os_3(CO)_{10}(CNPr)_2$ (**2a**) indicates that CO ligands are also fluxional in solution at room temperature (two broad peaks at δ 187.0 and 176.2), but exhibits four lines at δ 187.1, 186.1, 175.6 and 174.2 of intensity ratio 2:2:2:4 at $-50°C$, demonstrating that the *trans*-diaxial isomer is sterically more favourable than other isomers in solution at low temperature.

2.3. Reactivity of phosphine imide with $Os_3(CO)_{12}$

In contrast to the high yields noted in preparation of **1a–1d**, it proved difficult to prepare $Os_3(CO)_{11}(CN^tBu)$ via the deoxygenation of CO by phosphine imide. Treatment of $Os_3(CO)_{12}$ with $Ph_3P{=}N^tBu$ in CH_2Cl_2

at room temperature or under refluxing conditions shows no noticeable change of the reactants to give the expected product.

It is noteworthy to compare the reactivity of $Ph_3P{=}NR$ (R = Pr, ^{i}Pr, ^{t}Bu, Ph, CH_2Ph) with $Os_3(CO)_{12}$. The rate of the reaction decreases as the steric hindrance increases, *i.e.* Pr > ^{i}Pr > ^{t}Bu. The geometrical effect is likely to play a key role in determining the reactivity of phosphine imides. The reaction rate also decreases in the order Pr > CH_2Ph > Ph, indicating that a subtle electronic effect is also important. $Ph_3P{=}NPh$, being a more weakly nucleophilic reagent due to the electron withdrawing phenyl group, reacts very slowly with $Os_3(CO)_{12}$ in refluxing benzene over a period of one week to form isocyanide complexes. The reaction of $Os_3(CO)_{10}(CNCH_2Ph)_2$ with phosphine imide is in agreement with the importance of the electronic effect.

In contrast to the method of Mays [2], the present synthetic approach via the ylide type reaction is complementary and has the advantage of proceeding under milder conditions with high yield. Our results reveal that the ylide type deoxygenation reaction of $Os_3(CO)_{12}$ by phosphine imides can provide an alternative facile route to the synthesis of mono- and diisocyanide osmium complexes.

2.4. Preparation of $Ru_3(CO)_{11}(CNR)$

Treatment of $Ru_3(CO)_{12}$ with $Ph_3P{=}NR$ in CH_2Cl_2 at room temperature gives $Ru_3(CO)_{11}(CNR)$ (**4a**, R = Pr; **4b**, R = ^{i}Pr; **4c**, R = CH_2Ph) (eqn. (4)). The infrared spectrum of **4a** shows the ν(CN) absorption at 2193 cm^{-1} which is characteristic of terminally coordinated isocyanide ligand [12]. The FAB mass spectrum of **4a** shows the molecular ion at 683 as well as the subsequent CO-lost fragments. $Ph_3P{=}NPr$ shows good reactivity toward $Ru_3(CO)_{12}$, the complex $Ru_3(CO)_{11}$-(CNPr) was isolated in very high yield. $Ph_3P{=}NPh$ with a weaker nucleophilicity than $Ph_3P{=}NPr$ reacts with $Ru_3(CO)_{12}$ in refluxing benzene over two weeks to

$$Ru_3(CO)_{12} \xrightarrow[CH_2Cl_2,\ r.t.]{Ph_3P=NR} Ru_3(CO)_{11}(CNR) \quad (4)$$

4a, R = Pr, 92%
4b, R = ^{i}Pr, 38%
4c, R = CH_2Ph, 53%

afford $Ru_3(CO)_{11}(CNPh)$ in moderate yield. In these reactions, the yields of the products depend upon the bulk as well as the nucleophilicity of R in the imide $Ph_3P{=}NR$, as observed in the case of $Os_3(CO)_{11}(CNR)$ complexes.

3. Experimental section

3.1. General data

The complexes $Ph_3P{=}NPh$, $Ph_3P{=}N^tBu$, $Ph_3P{=}NPr$, $Ph_3P{=}N^iPr$ were prepared as reported previously [9,13]. Other reagents were purchased from commercial sources and were used as received. All reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques. Purifications were carried out in air if exposure was limited to a few hours. Solvents were dried by stirring over Na/benzophenone (diethyl ether) or CaH_2 (hexane, CH_2Cl_2, ethyl acetate) and freshly distilled prior to use. IR spectra were recorded with a Perkin-Elmer 882 infrared spectrophotometer. NMR spectra were obtained with a Bruker MSL-200, an AC-200, or an AMX-500 FT NMR spectrometer, and mass spectra with a VG 70-250S mass spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyser.

3.2. Reaction of $Os_3(CO)_{12}$ with $Ph_3P{=}NPr$

The complex $Os_3(CO)_{12}$ (120 mg, 0.13 mmol) was dissolved in CH_2Cl_2 (150 ml). A CH_2Cl_2 solution (10 ml) of $Ph_3P{=}NPr$ (54 mg, 0.17 mmol) was added slowly over 1 h, and the solution stirred for 6 h at room temperature. The solvent was removed under vacuum and the residue chromatographed on a silica gel TLC plate with hexane as eluent to give $Os_3(CO)_{11}(CNPr)$ (**1a**) (116 mg, 0.12 mmol, 92%) and $Os_3(CO)_{10}(CNPr)_2$ (**2a**) (6 mg, 0.005 mmol, 4%). $Os_3(CO)_{11}(CNPr)$ (**1a**): Anal. Calcd for $C_{15}H_7NO_{11}Os_3$: C, 19.01; H, 0.74. Found: C, 19.11; H, 0.72%. IR (n-hex): ν(CN) = 2195vw, ν(CO) = 2103w, 2056s, 2043vs, 2025m, 2007s, 1992m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.98 (t, 2H, CH_2), 1.76 (m, 2H, CH_2), 1.04 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 183.2 (br, CO), 173.3 (br, CO), 172.0 (br, CO), 120.9 (CN), 47.1 (CH_2), 22.6 (CH_2), 11.0 (CH_3); [δ 186.1, 184.3, 183.6, 173.4, 171.9 (CO, with intensity ratio of 2:2:1:4:2), 118.8 (CN), 46.9 (CH_2), 22.3 (CH_2), 11.2 (CH_3), at −50°C]. $Os_3(CO)_{10}(CNPr)_2$ (**2a**): IR (n-hex): ν(CN) = 2191w, ν(CO) = 2086vw, 2027vs, 1988s, 1969m, 1961sh cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.95 (t, 4H, CH_2), 1.75 (m, 4H, CH_2), 1.04 (t, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 187.0 (br, CO), 176.2 (br, CO), 122.7 (2 CN), 46.9 (CH_2), 22.7 (CH_2), 11.0 (CH_3); [δ 187.1, 186.1, 175.6, 174.2 (CO, with intensity ratio of 2:2:2:4), 119.9 (2 CN), 45.7 (CH_2), 21.4 (CH_2), 10.1 (CH_3), at −50°C].

3.3. Reaction of $Os_3(CO)_{12}$ with $Ph_3P{=}N^iPr$

The complex $Os_3(CO)_{12}$ (150 mg, 0.16 mmol) was dissolved in CH_2Cl_2 (200 ml). A CH_2Cl_2 solution (10 ml) of $Ph_3P{=}N^iPr$ (64 mg, 0.20 mmol) was added over 30 min, and the solution was stirred for 5 days at room temperature. The solvent was removed under vacuum and the residue was chromatographed on a silica gel TLC plate with hexane as eluent to give $Os_3(CO)_{11}$-(CN^iPr) (**1b**) (138 mg, 0.15 mmol, 88%). Anal. Calcd for $C_{15}H_7NO_{11}Os_3$: C, 19.01; H, 0.74. Found: C, 19.07;

H, 0.65%. IR (n-hex): ν(CN) = 2185vw, ν(CO) = 2101w, 2055s, 2042vs, 2024m, 2006s, 1990m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.40 (m, 1H, NC*H*), 1.44 (d, 6H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 183.2 (br, *C*O), 173.5 (br, *C*O), 172.0 (br, *C*O), 119.0 (*C*N), 50.1 (*C*H$_3$), 22.9 (*C*H).

3.4. Reaction of $Os_3(CO)_{12}$ with Ph_3P=NPh

The complexes $Os_3(CO)_{12}$ (150 mg, 0.16 mmol) and Ph_3P=NPh (71 mg, 0.20 mmol) were stirred in benzene (200 ml) under gentle reflux over one week. The solvent was removed under vacuum and the residue was chromatographed on a silica gel TLC plate with 10:100 CH_2Cl_2:hexane to give the following bands in order of elution: the major complex $Os_3(CO)_{11}$(CNPh) (**1d**) (120 mg, 0.12 mmol, 74%), the minor complex $Os_3(CO)_{10}$(CNPh)$_2$ (**2d**) (24 mg, 0.02 mmol, 14%) and traces of unidentified complexes. $Os_3(CO)_{11}$(CNPh) (**1d**): Anal. Calcd for $C_{18}H_5NO_{11}Os_3$: C, 22.02; H, 0.51. Found: C, 22.11; H, 0.57%. IR (n-hex): ν(CN) = 2163vw, ν(CO) = 2098w, 2058s, 2043vs, 2025m, 2010s, 1992m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.30–7.76 (m, Ph). $Os_3(CO)_{10}$(CNPh)$_2$ (**2d**): IR (n-hex): ν(CN) = 2146w, ν(CO) = 2073vw, 2031vs, 1996s, 1982m, 1968sh cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.24–7.40 (m, Ph).

3.5. Attempted reaction of $Os_3(CO)_{12}$ with Ph_3P=N^{t}Bu

Treatment of $Os_3(CO)_{12}$ (30 mg, 0.031 mmol) with excess Ph_3P=N^{t}Bu (30 mg, 0.09 mmol) in CH_2Cl_2 (30 ml) at room temperature or under refluxing conditions for a week gave no noticeable conversion of the reactants into the expected product.

3.6. Preparation of Ph_3P=NCH$_2$Ph

To an ice-cooled solution of triphenylphosphine dibromide (64.75 g, 0.153 mol) in CH_2Cl_2 was added simultaneously triethylamine (21.7 ml, 0.150 mol) and benzylamine (19.5 ml, 0.153 mol) over a period of 30 min. Stirring was continued for an additional hour and the precipitate was collected and washed with diethyl ether followed by ice-cold water to remove triethylamine hydrobromide. The remaining solid was crystallized from a CH_2Cl_2/ethyl acetate mixture to give benzylaminotriphenylphosphonium bromide (56.68 g, 0.126 mol).

To a stirred solution of the latter complex (56.68 g, 0.126 mol) in 300 ml of liquid ammonia was added sodium amide (5.44 g, 0.139 mol). The resulting mixture was stirred for another 30 min, and ammonia was evaporated. The remaining solid containing the phosphine imide and sodium bromide was extracted with diethyl ether and the remaining solid then extracted with 50:50 ether/CH_2Cl_2. The extracts were combined and the solvent removed under vacuum. The resultant solid was recrystallized from hexane/CH_2Cl_2 to give Ph_3P=NCH$_2$Ph (22.6 g, 0.062 mol), 49%). Anal. Calcd for $C_{25}H_{22}NP$: C, 81.74; H, 5.99. Found: C, 81.32; H, 6.40%.

3.7. Reaction of $Os_3(CO)_{12}$ with Ph_3P=NCH$_2$Ph

The complex $Os_3(CO)_{12}$ (402 mg, 0.44 mmol) was dissolved in CH_2Cl_2 (400 ml). A CH_2Cl_2 solution (10 ml) of Ph_3P=NCH$_2$Ph (215 mg, 0.576 mmol) was added over 2 h, and the solution was stirred for 2 days at room temperature. The solvent was removed under vacuum and the residue was chromatographed on a silica gel TLC plate with hexane as eluent to give $Os_3(CO)_{11}$(CNCH$_2$Ph) (**1c**) (364 mg, 0.37 mmol, 83%) and $Os_3(CO)_{10}$(CNCH$_2$Ph)$_2$ (**2c**) (57 mg, 0.05 mmol, 11%). $Os_3(CO)_{11}$(CNCH$_2$Ph) (**1c**): Anal. Calcd for $C_{19}H_7NO_{11}Os_3$: C, 22.91; H, 0.71. Found: C, 22.90; H, 0.74%. IR (CH_2Cl_2): ν(CN) = 2198vw, ν(CO) = 2102w, 2053vs, 2041vs, 2020m, 2009s, 1982m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.43–7.23 (m, Ph), 5.25 (s, 2H, CH_2). $Os_3(CO)_{10}$(CNCH$_2$Ph)$_2$ (**2c**): IR (CH_2Cl_2): ν(CN) = 2185w, ν(CO) = 2075vw, 2031vs, 2026vs, 1988s, 1968m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.43–7.24 (m, Ph), 5.21 (s, 2H, CH_2). MS (FAB): *m/z* 1087 (M^+), 996 (M^+ – CH_2Ph), 970 (M^+ – CNCH$_2$Ph), 942 (M^+ – CO – CNCH$_2$Ph).

3.8. Reaction of $Os_3(CO)_{10}(CNCH_2Ph)_2$ with Ph_3P=N-CH$_2$Ph

The complex $Os_3(CO)_{10}$(CNCH$_2$Ph)$_2$ (80 mg, 0.09 mmol) and Ph_3P=NPr (68 mg, 0.18 mmol) were stirred in refluxing benzene (100 ml) for 12 days. The solvent was removed under vacuum and the residue was chromatographed on a silica gel TLC plate with 40:100 CH_2Cl_2:hexane as eluent to afford $Os_3(CO)_9$(CNCH$_2$Ph)$_3$ (**3b**) (20 mg, 0.17 mmol, 19%). IR (CH_2Cl_2): ν(CN) = 2176m, ν(CO) = 2057vw, 2042vw, 2014vs, 1971m, 1954sh cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.38–7.24 (m, Ph), 5.10 (s, 6H, CH_2).

3.9. Reaction of $Os_3(CO)_{10}(CNCH_2Ph)_2$ with Ph_3P=N-Pr

The complexes $Os_3(CO)_{10}$(CNCH$_2$Ph)$_2$ (100 mg, 0.09 mmol) and Ph_3P=NCH$_2$Ph (59 mg, 0.18 mmol) were stirred in refluxing benzene (100 ml) for 10 days. The solvent was removed under vacuum and the residue chromatographed on a silica gel TLC plate with 20:100 CH_2Cl_2:hexane as eluent to afford $Os_3(CO)_9$(CNCH$_2$Ph)$_2$(CNPr) (**3a**) (24 mg, 0.023 mmol, 25%). IR (CH_2Cl_2): ν(CN) = 2178m, ν(CO) = 2055vw, 2042vw, 2014vs, 1972m, 1954sh cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.39–7.26 (m, Ph), 5.14 (s, 4H, C*H*$_2$Ph), 3.81 (t, 2H, CH_2), 1.69 (m, 2H, CH_2), 0.98 (t, 3H, CH_3).

3.10. Reaction of $Ru_3(CO)_{12}$ with $Ph_3P{=}NPr$

The complex $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) was dissolved in CH_2Cl_2 (200 ml). A CH_2Cl_2 solution (10 ml) of $Ph_3P{=}NPr$ (116 mg, 0.35 mmol) was added slowly over 1 h, and the solution stirred for 2 days at room temperature. The solvent was removed under vacuum and the residue chromatographed on a silica gel TLC plate with hexane as eluent to give $Ru_3(CO)_{11}(CNPr)$ (**4a**) (196 mg, 0.29 mmol, 92%). Anal. Calcd for $C_{15}H_7NO_{11}Ru_3$: C, 26.33; H, 0.99. Found: C, 26.48; H, 1.04%. IR (CH_2Cl_2): ν(CN) = 2193w, ν(CO) = 2094w, 2045vs, 2038vs, 2009s, 1998m cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.80 (t, 2H, CH_2), 1.81 (m, 2H, CH_2), 1.05 (t, 3H, CH_3). MS (FAB): m/z 683 (M^+), 655 (M^+ − CO), 627 (M^+ − 2CO), 599 (M^+ − 3CO), 571 (M^+ − 4CO), 543 (M^+ − 5CO), 515 (M^+ − 6CO), 587 (M^+ − 7CO), 459 (M^+ − 8CO).

3.11. Reaction of $Ru_3(CO)_{12}$ with $Ph_3P{=}N^iPr$

The complex $Ru_3CO)_{12}$ (202 mg, 0.32 mmol) was dissolved in CH_2Cl_2 (200 ml). A CH_2Cl_2 solution (10 ml) of $Ph_3P{=}N^iPr$ (116 mg, 0.35 mmol) was added over 1 h, and the solution stirred for 2 days at room temperature. The solvent was removed under vacuum and the residue chromatographed on a silica gel TLC plate with hexane as eluent to give $Ru_3(CO)_{11}(CN^iPr)$ (**4b**) (80 mg, 0.12 mmol, 38%). IR (CH_2Cl_2): ν(CN) = 2184w, ν(CO) = 2094w, 2046vs, 2008s, 1994m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.21 (m, 1H, NC*H*), 1.45 (d, 6H, CH_3).

3.12. Reaction of $Ru_3(CO)_{12}$ with $Ph_3P{=}NPh$

The complex $Ru_3(CO)_{12}$ (323 mg, 0.50 mmol) and $Ph_3P{=}NPh$ (214 mg, 0.61 mmol) were stirred in benzene (200 ml) under gentle reflux. After 4 days an additional quantity of $Ph_3P{=}NPh$ (114 mg in 20 ml of benzene) was added and the solution stirred in refluxing benzene for 10 more days. The solvent was removed under vacuum and the residue chromatographed on a silica gel TLC plate with 10:100 CH_2Cl_2:hexane to give the complex $Ru_3(CO)_{11}(CNPh)$ (**4d**) (143 mg, 0.20 mmol, 41%). IR (CH_2Cl_2): ν(CN) = 2156w, ν(CO) = 2090m, 2047vs, 2040vs, 2020m, 2010m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.45–7.23 (m, Ph). MS (FAB): m/z 717 (M^+), 657 (M^+ − 2CO), 641 (M^+ − Ph), 613 (M^+ − CO − Ph), 585 (M^+ − 2CO − Ph).

3.13. Reaction of $Ru_3(CO)_{12}$ with $Ph_3P{=}NCH_2Ph$

The complex $Ru_3(CO)_{12}$ (640 mg, 1.00 mmol) was dissolved in CH_2Cl_2 (500 ml). A CH_2Cl_2 solution (30 ml) of $Ph_3P{=}NCH_2Ph$ (773 mg, 2.10 mmol) was added over 2 h, and the solution was stirred for 8 days at room temperature. The solvent was removed under vacuum and the residue was chromatographed on a silica gel TLC plate with hexane as eluent to give $Ru_3(CO)_{11}(CNCH_2Ph)$ (**4c**) (384 mg, 0.53 mmol, 53%). IR (CH_2Cl_2): ν(CN) = 2189w, ν(CO) = 2095w, 2047vs, 2040s, 2007s, 1998sh cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.46–7.25 (m, Ph), 5.06 (s, 2H, CH_2). MS (FAB): m/z 731 (M^+), 703 (M^+ − CO), 675 (M^+ − 2CO), 647 (M^+ − 3CO), 619 (M^+ − 4CO), 591 (M^+ − 5CO), 563 (M^+ − 6CO), 535 (M^+ − 7CO), 507 (M^+ − 8CO), 479 (M^+ − 9CO).

Acknowledgment

We thank the National Science Council of the Republic of China for financial support.

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