Inorganica Chimica Acta, *212* (1993) 303-310

Selective substitution and oxidative addition reactions at the iridium vertex in $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ and related clusters

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(Received February 9, 1993; revised April 29, 1993)

Abstract

The heterobimetallic cluster complex $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ undergoes a variety of reactions (e.g. with carbon monoxide, phosphines, phenylacetylene, hydrosilanes and alkyl halides) selectively at the iridium vertex to give substitution and oxidative addition products. $[PPN]^+$ and/or $[Et_4N]^+$ salts of several cluster derivatives, such as $[Re_7C(CO)_{21}Ir(L)(CO)]^{2-}$ (L = CO, $PMePh_2$ and PPh_3), $[Re_7C(CO)_{21}Ir(H)(SiPh_3)(CO)]^{2-}$ and $[Re_7C(CO)_{21}Ir(\eta^3\text{-}C_3H_5)(CO)]^-$ have been isolated and fully characterized by analytical and spectroscopic data. $[Re_7C(CO)_{21}Ir(CO)_2]^{2-}$ and $[Re_7C(CO)_{21}Ir(H)(SiPh_3)(CO)]^{2-}$ also react selectively with tertiary phosphines to afford the $PMePh_2$ and PPh_3 derivatives $[Re_7C(CO)_{21}Ir(CO)(PR_3)]^{2-}$, respectively.

Introduction

Oxidative addition is a fundamental reaction type in organometallic chemistry, and the concept was first developed in relation to the reactivity toward small molecules displayed by the square planar iridium(I) compound, *trans*-$Ir(CO)(PPh_3)_2Cl$, or 'Vaska's complex' [1]. Important oxidative addition reactions also occur with non-planar, cyclopentadienyl iridium(I) centers, e.g. the reactions of halogens and alkyl halides with $CpIr(CO)(PPh_3)$ [2] and of methyl iodide with $CpIr(C_8H_{14})(PPr_3')$ [3]. Furthermore, a great deal of attention has been focused in recent years on compounds of the type $(\eta^5\text{-}C_5R_5)Ir(PMe_3)H_2$ and $(\eta^5\text{-}C_5R_5)Ir(CO)_2$, where R = H and Me, which provide reactive intermediates that can activate alkane C–H bonds [4].

In previous work we have applied capping reactions to $[Re_7C(CO)_{21}]^{3-}$ in order to synthesize a set of mixed-metal clusters $[Re_7C(CO)_{21}ML_n]^{2-}$, and we have explored the properties of these compounds in relation to the formally analogous set of Cp^- derivatives $CpML_n$ [5]. In view of the importance of the iridium compounds CpIrLL′, we have been particularly interested in examining the reactivity of analogous {Re₇}IrLL′ clusters. In this paper we report oxidative addition and ligand substitution reactions that occur selectively at the iridium center in $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ [5e]. Transformations leading to well-characterized products are summarized in Scheme 1. A portion of these results was presented in an earlier communication [6].

Experimental

General procedures

All reactions were carried out under a nitrogen atmosphere and were monitored by their IR (ν(CO)) spectra. All reaction solvents were distilled from appropriate drying agents and were deoxygenated immediately before use. $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ was prepared as previously described [5e]; ^{13}CO-enriched samples were prepared from ^{13}CO-enriched $[PPN]_3[Re_7C(CO)_{21}]$ [7] and non-enriched $[Ir(C_8H_{14})_2(CO)Cl]_2$ [8]. Carbon monoxide (Linde) and acetylene (Matheson) were research grade gases. Methyldiphenylphosphine, triphenylphosphine, phenylacetylene, triphenylsilane, diphenylsilane and methyl iodide were obtained from Aldrich Chemical Co; allyl bromide was obtained from Matheson, Coleman and Bell and 1,2-dichloroethane from Fisher Scientific. All commercial samples were used as received.

IR spectra were recorded with a Perkin-Elmer 1750 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were obtained with General Electric QE-300 (300.0 MHz for ^1H and 75.5 MHz for ^{13}C) or GN-500 spectrometers (500 MHz for ^1H and 125 MHz for ^{13}C), using the proton and carbon resonances of deuteriated solvents as chemical shift references. ^{13}P NMR spectra were acquired on a General Electric GN-300NB instrument

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0020-1693/93/$6.00

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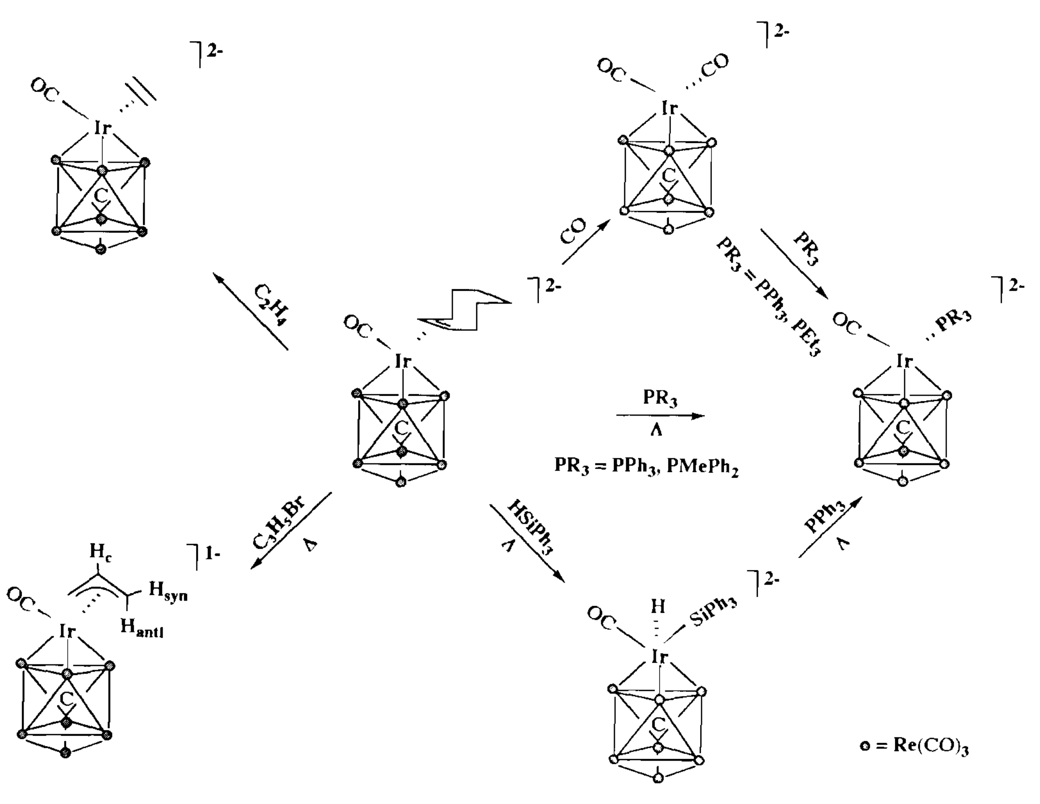

Scheme 1.

at 121.5 MHz and chemical shift values were referenced to external 85% H_3PO_4. Negative ion fast atom bombardment mass spectra (FAB-MS) and elemental analyses were obtained by the respective staffs of the Mass Spectrometry Center and the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois.

Synthesis of $[PPN]_2[Re_7C(CO)_{21}Ir(CO)_2]$

$[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ (19.0 mg, 0.00574 mmol) was dissolved in dichloromethane (*c.* 30 ml) in a 250 ml heavy-walled glass pressure bottle. The bottle was filled with carbon monoxide to 20 psig, and the solution was stirred at ambient temperature for 12 h. The bottle was then vented, and the solution was filtered into a Schlenk tube. The volume of the solution was reduced to *c.* 1 ml under vacuum, and 2-propanol was carefully layered on top. Overnight standing at room temperature gave dark red crystals (10.3 mg, 56%). *Anal.* Calc. for $C_{96}H_{60}N_2IrO_{23}P_4Re_7$: C, 35.71; H, 1.87; N, 0.87. Found: C, 35.87; H, 2.04; N, 0.82%. IR (acetone): ν(CO) 2059(vw), 2043(w), 2014(s), 2001(vs), 1944(w), 1931(w), 1890(w) cm^{-1}. ^{13}C NMR (acetone-d_6, 20 °C): δ 431.5 (s, μ_6-*C*), 204.0 (s, 3C, $Re(CO)_3$), 192.8 (s, 9C), 191.3 (s, 9C), 181.6 (s, 2C, Ir–*C*O). FAB-MS (negative ion): *m*/*z* (^{187}Re, ^{193}Ir) 2696 (*M* − PPN), 2158 (*M* − 2PPN), 1909 (*M* − 2PPN − $Ir(CO)_2$).

Synthesis of $[PPN]_2[Re_7C(CO)_{21}Ir(CO)(PMePh_2)]$

$[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ (39.4 mg, 0.0119 mmol) was dissolved in acetone (*c.* 20 ml). Methyldiphenylphosphine (4.4 μl, 0.0240 mmol) was added to the solution, which was brought to reflux and maintained there for 2.5 h. The solution was allowed to cool to room temperature, and the solvent was removed under vacuum. The residue was dissolved in dichloromethane (2 ml), and ethyl alcohol was layered on top. A black powder was deposited after ten days at room temperature (21.0 mg, 69%). *Anal.* Calc. for $C_{108}H_{73}N_2IrO_{22}P_5Re_7$: C, 38.14; H, 2.16; N, 0.82. Found: C, 37.75; H, 2.67; N, 0.70%. IR (acetone): ν(CO) 2044(w), 1993(vs), 1973(w, sh), 1942(w), 1920(w), 1884(vw) cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 8.00–7.40 (m, C_6H_5), 2.58 (d, ^2J(P–H) = 11.1 Hz, $P(CH_3)(C_6H_5)_2$). ^{31}P NMR ($CDCl_3$, 20 °C): 21.6 ppm (s, 4P, *P*Ph_3 in PPN^+), 8.7 ppm (m, 1P, Ir-*P*$MePh_2$). FAB-MS (negative ion): *m*/*z* (^{187}Re, ^{193}Ir) 2868 (*M* − PPN), 2668 (*M* − PPN − $PMePh_2$), 2330 (*M* − 2PPN), 2130 (*M* − 2PPN − $PMePh_2$).

Synthesis of $[PPN]_2[Re_7C(CO)_{21}Ir(CO)(PPh_3)]$

$[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ (24.3 mg, 0.00734 mmol) was dissolved in THF, and PPh_3 (4.1 mg, 0.0156 mmol) was added. The solution was heated to reflux for 2 h and then evaporated under vacuum. The residue was dissolved in dichloromethane, and 2-propanol solvent diffusion over a period of 10 days gave a very small amount of black solid. *Anal.* Calc. for $C_{113}H_{75}N_2IrO_{22}P_5Re_7$: C, 39.19; H, 2.18; N, 0.81. Found: C, 38.23; H, 2.40; N, 0.77%. Ir (acetone): ν(CO) 2044(w), 1993(vs), 1973 (w, sh), 1935(w), 1920(w), 1886(w) cm^{-1}. ^{13}C NMR (acetone-d$_6$, 0 °C): δ 204.6 (s, 3C), 197.7 (s, 9C), 192.1 (s, 9C), 181.4 (d, 1C, ^2J(P–C) = 15.1 Hz, Ir–*C*O). ^{31}P NMR (CDCl$_3$, 20 °C): 30.2 ppm (s, 1P, Ir–*P*Ph$_3$), 22.2 ppm (s, 4P, *P*Ph$_3$ in PPN$^+$). FAB-MS (negative ion): *m/z* (^{187}Re, ^{193}Ir) 2930 ($M-$PPN), 2392 ($M-2$PPN), 2130 ($M-2$PPN $-$ PPh$_3$).

Synthesis of $[PPN]_2[Re_7C(CO)_{21}Ir(H)(CO)(SiPh_3)]$

A THF solution of $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ (53 mg, 0.016 mmol) and HSiPh$_3$ (6.4 mg, 0.025 mmol) was heated to reflux for 4 h. The solvent was removed *in vacuo* and the residue was crystallized from dichloromethane/2-propanol by solvent diffusion. A black microcrystalline solid was isolated (42 mg, 77%). IR (acetone): ν(CO) 2053(w), 2043(vw), 2003(vs), 1983(w, sh), 1946(w), 1926(w), 1889(vw) cm^{-1}. ^{1}H NMR (acetone-d$_6$, 20 °C): δ 8.00–7.20 (m, 75H, C$_6$*H*$_5$), -15.70 (s, 1H, Ir–*H*). ^{13}C NMR (dichloromethane-d$_2$, 0 °C): δ 204.1 (s, 3C), 192.1 (s, 9C), 191.0 (s, 9C), 174.0 (d, 1C, ^2J(C–H) = 4.6 Hz, Ir–*C*O). FAB-MS (negative ion): *m/z* (^{187}Re, ^{193}Ir) 2928 ($M-$PPN), 2668 ($M-$PPN $-$ HSiPh$_3$), 2130 ($M-2$PPN $-$ HSiPh$_3$).

Synthesis of $[Et_4N]_2[Re_7C(CO)_{21}Ir(H)(SiPh_3)(CO)]$

THF (*c.* 40 ml) was added to $[Et_4N]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ (19.5 mg, 0.00782 mmol) and HSiPh$_3$ (2.4 mg, 0.00922 mmol), and the resulting solution was heated under reflux for 5 h. The solvent was removed under vacuum, the residue was washed with cyclohexane, and then it was dissolved in acetone. 2-Propanol was carefully layered on top of the solution, and the tube containing it was left at room temperature for 4 days. A black powder that formed was collected (4.2 mg, 20%). *Anal.* Calc. for $C_{57}H_{56}N_2IrO_{22}Re_7$: C, 25.89; H, 2.13; N, 1.06. Found: C, 25.71; H, 1.95; N, 1.01%. ^{1}H NMR (acetone-d$_6$, 20 °C): δ 7.85–7.20 (m, 15H, *H* in SiPh$_3$), -15.7 (s, 1H, Ir–*H*). FAB-MS (negative ion): *m/z* (^{187}Re, ^{193}Ir) 2520 ($M-$Et$_4$N), 2390 ($M-2$Et$_4$N), 2260 ($M-$Et$_4$N $-$ HSiPh$_3$), 2130 ($M-2$Et$_4$N $-$ HSiPh$_3$).

Synthesis of $[PPN][Re_7C(CO)_{21}Ir(\eta^3\text{-}C_3H_5)(CO)]$

A THF solution of $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ (95 mg, 0.029 mmol) and allyl bromide (5.0 μl, 0.058 mmol) was heated to reflux for 2 h. After evaporation of the solvent, the black mixture was separated on a deactivated (5% H$_2$O) neutral alumina column with dichloromethane as the eluant. A red–brown band was eluted first, from which $[PPN][Re_7C(CO)_{21}Ir(\eta^3\text{-}C_3H_5)(CO)]$ was isolated after crystallization from chloroform–pentane by solvent diffusion (33 mg, 40%). *Anal.* Calc. for $C_{63}H_{36}Cl_3NIrO_{22}P_2Re_7$ ($[PPN][Re_7C(CO)_{21}Ir(\eta^3\text{-}C_3H_5)(CO)]\cdot CHCl_3$): C, 26.80; H, 1.29; N, 0.50; Cl, 3.77. Found: C, 27.07; H, 1.38; N, 0.44; Cl, 3.93%. IR (acetone): ν(CO) 2066(w), 2026(m), 2014(vs), 1989(w), 1965(w), 1942(w), 1896(vw) cm^{-1}. ^{1}H NMR (CDCl$_3$, 20 °C): δ 7.80–7.40 (m, C$_6$H$_5$), 5.49 (m, 1H, H$_c$, J(H$_c$, H$_{anti}$) = 11.0 Hz, J(H$_c$, H$_{syn}$) = 6.3 Hz, J(H$_{gem}$) not resolved), 3.49 (d, 2H, H$_{syn}$), 3.10 (d, 2H, H$_{anti}$) ^{13}C NMR (CDCl$_3$, 20 °C): δ 431.0 (s, μ_6-*C*), 200.6 (s, 3C), 188.8 (s, 9C), 188.0 (s, 9C), 158.6 (s, 1C, Ir–*C*O). FAB-MS (negative ion): *m/z* (^{187}Re, ^{193}Ir) 2668 ($M-$C$_3$H$_5$), 2171 ($M-$PPN), 2130 ($M-$PPN $-$ C$_3$H$_5$).

Reaction of $[PPN]_2[Re_7C(CO)_{21}Ir(CO)_2]$ *with* $PMePh_2$

$[PPN]_2[Re_7C(CO)_{21}Ir(CO)_2]$ (4.8 mg, 0.0015 mmol) was dissolved in acetone (10 ml) and PMePh$_2$ (2.2 μl, 0.012 mmol) was added to the solution. The mixture was stirred at room temperature for 48 h, after which time the IR spectrum showed only the carbonyl bands for $[PPN]_2[Re_7C(CO)_{21}Ir(CO)(PMePh_2)]$.

Reaction of $[PPN]_2[Re_7C(CO)_{21}Ir(H)(CO)(SiPh_3)]$ *with* PPh_3

To an acetone solution (*c.* 30 ml) of $[PPN]_2[Re_7C(CO)_{21}Ir(H)(CO)(SiPh_3)]$ (5.1 mg, 0.0015 mmol) was added PPh$_3$ (0.5 mg, 0.0017 mmol). The solution was heated and kept under reflux for 7 h. Only the bands for $[PPN]_2[Re_7C(CO)_{21}Ir(CO)(PPh_3)]$ were identified in the solution IR spectrum. The ^{1}H NMR spectrum also showed disappearance of the hydride signal.

Reaction of $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ *with phenylacetylene*

To an acetone solution (*c.* 15 ml) of $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ (39.1 mg, 0.0118 mmol) was added phenylacetylene (6.5 μl, 0.0598 mmol). The solution was maintained at room temperature for 24 h, during which period the color changed from dark red to greenish brown. The solvent was removed *in vacuo*, and the residue was purified by dichloromethane/2-propanol solvent diffusion at room temperature. A black powder (18.5 mg, 47%) was isolated after two weeks. *Anal.* Calc. for $C_{103}H_{66}N_2IrO_{22}P_4Re_7$ ($[PPN]_2[Re_7C(CO)_{21}Ir(PhCCH)(CO)]$): C, 37.45; H, 2.01; N, 0.85. Found: C, 37.04; H, 2.24; N, 0.79%. IR (acetone): ν(CO) 2050 (vw), 2013(m), 2003(s), 1992(vs), 1941(w, sh), 1933(vw), 1920(w), 1893(vw, sh) cm^{-1}. ^{1}H NMR (CDCl$_3$, 20 °C): δ 9.13 (s, 1H), 7.70–7.30 (m, > 60H, C$_6$*H*$_5$ in PPN$^+$). FAB-MS (negative ion): *m/z* (^{187}Re, ^{193}Ir) 2770 ($M-$PPN), 2668 ($M-$PPN $-$ PhCCH), 2232 ($M-2$PPN).

Reaction of $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ *with 1,2-dichloroethane*

A 1,2-dichloroethane solution of $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ was heated to reflux for 4 h. After the solvent was removed *in vacuo*, the residue was dissolved in dichloromethane, and then a layer of 2-propanol was added. A black powder was isolated after 2 days. IR (acetone): ν(CO) 2022(s), 2009(vs), 1996(m), 1919(w-m, br). FAB-MS (negative ion): *m/z* (^{187}Re, ^{193}Ir) 2760 ($[PPN][Re_7C(CO)_{21}Ir(Cl)(CH_2CH_2Cl)(CO)]$), 2694 ($[PPN][Re_7C(CO)_{21}Ir(Cl)(CO)]$), 2224 ($[Re_7C(CO)_{21}Ir(Cl)(CH_2CH_2Cl)(CO)]$), 2158 ($[PPN][Re_7C(CO)_{21}Ir(Cl)(CO)]$).

Attempted reaction of $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ with CH_3I

$[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ (12.2 mg, 0.00368 mmol) was dissolved in dichloromethane (*c.* 15 ml) and to this solution was added methyl iodide (4.4 μl, 0.0707 mmol). The solution was stirred at room temperature and its IR spectrum was monitored. Broadening of the most intense IR band of the starting material at 1996 cm^{-1} was observed after 4 days. An additional amount of methyl iodide (3.3 μl, 0.0530 mmol) was added to the solution. After one week, a mixture of the starting material and a new species having major IR (ν(CO)) bands at 2021(m) and 2006(vs) cm^{-1} was observed. Waiting another week did not appear to afford any change in the conversion of starting material. No attempt was made to isolate the new product.

Results

Ligand substitution reactions of $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ $[Re_7C(CO)_{21}Ir(CO)_2]^{2-}$

We showed previously that the cyclooctene ligand in the mixed-metal cluster $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ is labile and can be replaced cleanly by ethylene under mild conditions [5e]. A similar reaction of $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ with carbon monoxide (20 psig) at ambient temperature for 12 h formed the carbonyl derivative $[Re_7C(CO)_{21}Ir(CO)_2]^{2-}$, which was isolated in 56% yield. This compound is an analog of the previously characterized $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ [5b]; however, the syntheses of these compounds follow different routes. $[Re_7(CO)_{21}Rh(CO)_2]^{2-}$ is prepared by a direct reaction of $[Re_7C(CO)_{21}]^{3-}$ and $[Rh(CO)_2Cl]_2$, but $[Re_7C(CO)_{21}Ir(CO)_2]^{2-}$ has not been obtained by direct capping of $[Re_7C(CO)_{21}]^{3-}$. A dimeric '$[Ir(CO)_2Cl]_2$' is not known, and the use of $Ir(CO)_2(p\text{-}CH_3C_6H_4NH_2)Cl$ as a capping reagent did not give the expected $[Re_7C(CO)_{21}Ir(CO)_2]^{2-}$ [9].

The general structure of this class of molecules has been substantiated by an X-ray crystallographic study of $[PPN]_2[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]$ [5e], which showed the anticipated 1,4-bicapped octahedral geometry of the metal core. An X-ray study of $[PPN]_2[Re_7C(CO)_{21}Ir(CO)_2]$ showed the same core geometry, but the crystal suffered from a severe center-of-symmetry disorder problem that limited the accuracy of the results, so the details will not be reported here [10].

The two compounds $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ and $[Re_7C(CO)_{21}Ir(CO)_2]^{2-}$ have very similar IR ν(CO) spectra. Two distinct bands are observed, at 2020(m) and 2000(s) cm^{-1} for the rhodium compound [5b] and at 2014(m) and 2001(s) cm^{-1} for the iridium compound. The higher frequency band is assumed to be due primarily to the capping $M(CO)_2$ moiety, probably the symmetric stretching combination. The lower frequency observed for the iridium carbonyl band parallels a similar relationship in mononuclear $CpIr(CO)_2$ and $CpRh(CO)_2$ [11].

For ^{13}C NMR studies, ^{13}CO-enriched samples of $[PPN]_2[Re_7C(CO)_{21}Ir(CO)_2]$ were prepared by three distinct routes, as shown in eqns. (1)–(3). In the first route, non-enriched $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ was allowed to react with pure ^{13}CO. The second route involved the reaction between moderately enriched (*c.* 20%) $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ and pure ^{13}CO. In the last method, enriched $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ was allowed to react with non-enriched carbon monoxide. ^{13}C NMR spectra of these three samples at room temperature are shown in Fig. 1.

$$[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-} + {}^{***}CO \longrightarrow [Re(CO)_3Re_6C({}^{**}CO)_{18}Ir({}^{**}CO)_2]^{2-} \tag{1}$$

$$[Re_7{}^{*}C({}^{*}CO)_{21}Ir(C_8H_{14})({}^{*}CO)]^{2-} + {}^{***}CO \longrightarrow [Re({}^{*}CO)_3Re_6{}^{*}C({}^{**}CO)_{18}Ir({}^{**}CO)_2]^{2-} \tag{2}$$

$$[Re_7{}^{**}C({}^{**}CO)_{21}Ir(C_8H_{14})({}^{**}CO)]^{2-} + CO \longrightarrow [Re({}^{**}CO)_3Re_6{}^{**}C({}^{*}CO)_{18}Ir({}^{*}CO)_2]^{2-} \tag{3}$$

* = slightly enriched, ** = moderately enriched, *** = highly enriched.

The ^{13}C NMR spectrum of $[PPN]_2[Re_7C(CO)_{21}Ir(CO)_2]$ from reaction (1) shows a 9:9:2 set of resonances for the carbonyls, which is part of the 3:9:9:2 pattern expected for the $[Re_7C(CO)_{21}ML_n]^{2-}$ complexes with 1,4-bicapped octahedral structure [5]. The observation of enrichment in the carbonyls on the rhenium sites implies carbonyl scrambling from the iridium center to the rhenium atoms after carbon monoxide substitution for cyclooctene. However, the absence of a carbonyl signal for the capping $Re(CO)_3$ group indicates that this scrambling process only occurs among the heterometal center and the six octahedral rhenium sites.

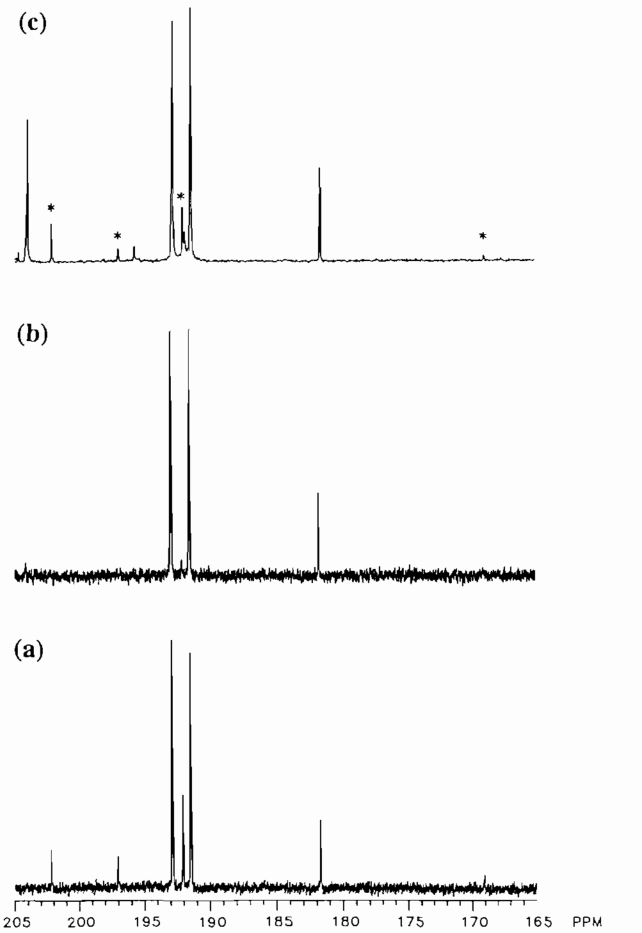

Fig. 1. Comparison of the ^{13}C NMR spectra (carbonyl region) of ^{13}CO enriched $[PPN]_2[Re_7C(CO)_{21}Ir(CO)_2]$ prepared via three different routes. Spectra (a), (b) and (c) correspond to samples obtained from reactions (1), (2) and (3), respectively. The peaks labelled with an asterisk are due to an isomer [10]

Similar behavior in $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ has been reported, i.e. the reaction of $[Re_7C(CO)_{21}]^{3-}$ with $[Rh(^{13}CO)_2Cl]_2$ leads to enrichment of carbonyls on all metal centers except the capping rhenium [12].

Observations of $[PPN]_2[Re_7C(CO)_{21}Ir(CO)_2]$ samples prepared via reactions (2) and (3) fully agree with the above conclusion. For an initially enriched $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ (*c*. 20%), reaction with pure ^{13}CO caused additional enrichment of the 18 carbonyls on the six octahedral rhenium sites. This result can be seen in the spectrum of the sample from reaction (2), in which the capping $Re(CO)_3$ carbonyl resonance is visible, but its intensity relative to the other three signals is much lower than the 3:9:9:2 ratio expected for a uniformly enriched species. Similarly, when a partially enriched $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ sample was treated with normal carbon monoxide in reaction (3), carbon monoxide exchange and scrambling caused decreased enrichment in 18 of the 21 carbonyls, as evidenced in the ^{13}C NMR spectrum by a relative intensity greater than 3 for the carbonyls on the capping rhenium center.

$[Re_7C(CO)_{21}Ir(CO)(PR_3)]^{2-}$

Reactions of $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ with tertiary phosphines, such as PPh_3 and $PMePh_2$, proceeded in boiling acetone or THF to form the phosphine ligand substituted products $[Re_7C(CO)_{21}Ir(CO)(PR_3)]^{2-}$, which were straightforwardly formulated on the basis of FAB mass spectrometry. It has not been possible to synthesize these compounds through direct capping of $[Re_7C(CO)_{21}]^{3-}$. An attempted reaction between $[Re_7C(CO)_{21}]^{3-}$ and $Ir(CO)(PPh_3)_2Cl$ did not give $[Re_7C(CO)_{21}Ir(CO)(PPh_3)]^{2-}$, apparently because the strong bonding of the phosphine ligands to the mononuclear iridium center did not allow the formation of an appropriate (formally 12 e^-) capping fragment [13].

Structural characterization of the phosphine ligand substituted products is based on the results of IR and ^{13}C NMR studies. The most intense IR band of $[Re_7C(CO)_{21}Ir(CO)(PR_3)]^{2-}$ is shifted 3–4 cm^{-1} to lower frequency compared with $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$, which is in agreement with the cyclooctene ligand being replaced by a stronger σ-donor phosphine ligand. The ^{13}C NMR spectrum obtained for $[PPN]_2[Re_7C(CO)_{21}Ir(CO)(PPh_3)]$ is shown in Fig. 2. The 3:9:9:1 pattern for the 22 carbonyl ligands is observed, and a 1,4-bicapped octahedral structure for the cluster is indicated. The carbonyl resonance at 181.4 ppm shows a two-bond coupling of 15.1 Hz to the phosphorus atom on the iridium center. This coupling constant is similar to the value of $^2J(P\text{–}C)$ in $[Re_7C(CO)_{21}Rh(CO)(PR_3)]^{2-}$ (~10 Hz) [12].

Reactions of $[Re_7C(CO)_{21}Ir(CO)_2]^{2-}$ with $PMePh_2$ and PEt_3

$[Re_7C(CO)_{21}Ir(CO)_2]^{2-}$ reacted slowly at ambient temperature over 2 days with methyldiphenylphosphine

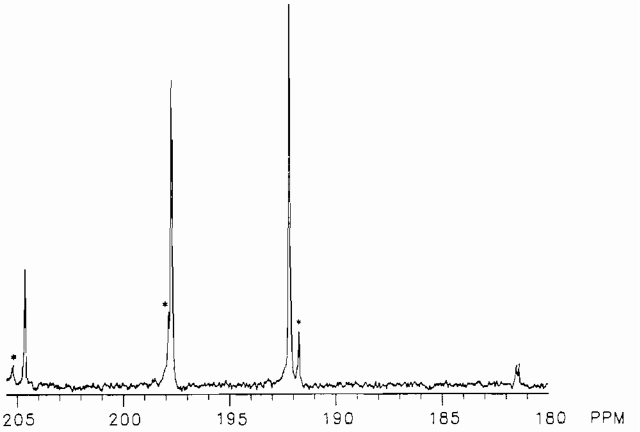

Fig 2. ^{13}C NMR spectrum (carbonyl region, acetone-d_6, 0 °C) of $[PPN]_2[Re_7C(CO)_{21}Ir(CO)(PPh_3)]$ Asterisks indicate unidentified impurities.

or triethylphosphine to form $[Re_7C(CO)_{21}Ir(CO)(PR_3)]^{2-}$ ($PR_3 = PMePh_2$, PEt_3). Although no effort was made to study the kinetics of these reactions, the apparent rates of carbonyl substitution by phosphines were much slower than those of the analogous reactions involving $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ [14]. It is worth noting that Schuster-Woldan and Basolo observed similar behavior in $CpRh(CO)_2$ and $CpIr(CO)_2$ and attributed it to a stronger Ir–C bond [15].

No reaction between $[Re_7C(CO)_{21}Ir(CO)_2]^{2-}$ and triphenylphosphine was observed at room temperature. When the mixture was heated in refluxing acetone, a reaction involving only the cluster compound was observed, which will be discussed in a separate publication [10].

Reactions between $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ and acetylenes

The reaction of $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ with acetylene in a closed system at ambient temperature gave a black powder after crystallization, whose IR spectrum showed an overall pattern similar to that of the starting material, but with the most intense CO band shifted to 1992 cm^{-1}. However, no acetylenic proton resonance could be found in the ^{1}H NMR spectrum amid strong counterion and solvent signals.

Substituting phenylacetylene for acetylene as a reactant resulted in the formation of a product that displayed two bands, at 2003(s) and 1993(vs) cm^{-1}, in its IR spectrum. In the negative ion FAB mass spectrum the most abundant peak was at m/z 2766, which corresponds to '$[PPN][Re_7C(CO)_{21}Ir(PhCCH)(CO)]$'. The ^{1}H NMR signal observed at the low-field position of δ 9.13 is consistent with a coordinated acetylene rather than the tautomeric vinylidene moiety. However, the higher frequency IR band may imply the presence of some of the hydrido-(phenyl)acetylide isomer, the product of oxidative addition. All of these species have been observed under various conditions in mononuclear compounds [16].

Oxidative addition reactions of $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$

$[Re_7C(CO)_{21}Ir(H)(CO)(SiPh_3)]^{2-}$

Heating $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ with hydrosilanes ($HSiEt_3$, $HSiPh_3$ and H_2SiPh_2) in refluxing acetone or THF for several hours led to a new species that displayed a shift of 7–8 cm^{-1} to higher frequency for the most intense carbonyl stretching band in the IR spectrum. $[Re_7C(CO)_{21}Ir(CO)_2]^{2-}$ formed when solvent diffusion crystallization was carried out on the diphenylsilane reaction mixture, suggesting that silane reductive elimination is facile. Only in the case of triphenylsilane was the oxidative addition product $[A]_2[Re_7C(CO)_{21}Ir(H)(SiPh_3)(CO)]$ ($A = PPN$ or Et_4N) isolated and fully characterized.

A signal at −15.7 ppm in the ^{1}H NMR spectrum was observed for $[Re_7C(CO)_{21}Ir(H)(SiPh_3)(CO)]^{2-}$ due to the hydride ligand on the iridium center. The question of possibly incomplete H–Si bond oxidative addition, which is frequently encountered in mononuclear systems [17], was addressed by careful examination of the base of the hydride signal. Under the experimental conditions ($S/N > 200$) that should allow observation of ^{29}Si satellites, no ^{29}Si–^{1}H coupling was observed (J(Si–H) < 16 Hz). This fact strongly implies a complete oxidative addition of the H–Si bond in $[Re_7C(CO)_{21}Ir(H)(SiPh_3)(CO)]^{2-}$. The ^{13}C NMR spectrum contains the usual 3:9:9:1 pattern with the highest field carbonyl resonance at δ 174.0 showing a small coupling of 4.6 Hz, which was confirmed as due to the hydride ligand by a selective ^{1}H decoupling experiment. Based on its relative intensity and chemical shift, this carbon resonance is assigned to the single carbonyl bound to iridium. Since no other coupling was observed in the ^{13}C NMR spectrum, the hydride ligand is probably bonded only to the iridium center.

The reaction of $[Re_7C(CO)_{21}Ir(H)(SiPh_3)(CO)]^{2-}$ with excess triphenylphosphine proceeded cleanly in refluxing acetone and gave $[Re_7C(CO)_{21}Ir(CO)(PPh_3)]^{2-}$ as the cluster product.

Attempts were made to replace the hydride ligand with a halogen atom. The reactions of $[Re_7C(CO)_{21}Ir(H)(SiPh_3)CO)]^{2-}$ with $CHBr_3$ and $CBrCl_3$ turned out to be complicated, with more than one product being observed in each crude reaction mixture, and only $[Re_7C(CO)_{21}Ir(CO)_2]^{2-}$ was isolated as a decomposition product.

$[Re_7C(CO)_{21}Ir(\eta^3\text{-}C_3H_5)(CO)]^-$

Heating $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ with allyl bromide in refluxing THF gave a reaction mixture that appeared to have two sets of independent IR bands in the carbonyl region between 2030 and 1980 cm^{-1}, indicating the formation of more than one product. When this reaction mixture was placed on a deactivated neutral alumina column and eluted with dichloromethane, only one red–brown band was eluted, and the oxidative addition product $[PPN][Re_7C(CO)_{21}Ir(\eta^3\text{-}C_3H_5)(CO)]$ was isolated as a black solid. Its solution IR spectrum shows a pattern rather different from the familiar pattern of one strong and five weak bands, with the observation of two major bands at 2026(m) and 2014(s) cm^{-1}. The wavenumber shift of 17 cm^{-1} to higher energy is consistent with a negative charge reduction of one unit [18].

The ^{1}H NMR spectrum of $[PPN][Re_7C(CO)_{21}Ir(\eta^3\text{-}C_3H_5)(CO)]$ consists of three sets of resonances for the allyl ligand. This implies that the allyl group adopts an η^3- instead of an η^1-coordination mode. The ^{13}C

NMR carbonyl resonances of [PPN][$Re_7C(CO)_{21}Ir(\eta^3$-$C_3H_5)(CO)$] are all shifted to higher field compared to those of the starting cluster compound, in agreement with the overall cluster charge reduction. ^{13}C NMR data further show that the η^3-allyl group must coordinate only to the iridium center, since the typical [5b, 7] 3:9:9 pattern of carbonyl resonances is observed for the (μ_6-C)$[Re(CO)_3]_7$ moiety, implying C_3 symmetry. Therefore, this allyl coordination mode is similar to that in $[Ph_4P][Rh_6(CO)_{14}(\eta^3\text{-}C_3H_5)]$ [19], but differs from the bridging mode reported for the carbido cluster $[PPN][Ru_6C(CO)_{15}(\mu_2,\eta^3\text{-}C_3H_5)]$ [20].

Other reactions between $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ and organic halides

Heating $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ with excess benzyl bromide or ethyl iodide in refluxing THF did not result in any reaction after several hours. Stirring $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ with excess methyl iodide at room temperature over a period of weeks only gave an incomplete reaction with the detection of a new species by IR spectroscopy (new bands at ~2020(m) and ~2010(vs) cm^{-1}). This pattern of IR bands was also observed when $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ was heated in neat 1,2-dichloroethane or in THF with excess acetyl chloride. Although in both cases the reactions were still incomplete when cluster degradation started to occur (indicated by the appearance of a medium to strong band at *c*. 1910–1920 cm^{-1}), the FAB-MS result on the former system suggested that the expected oxidative addition product $[Re_7C(CO)_{21}Ir(Cl)CH_2CH_2Cl)(CO)]^{2-}$ was present in the reaction mixture. The reaction between $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ and propargyl bromide ($HCCCH_2Br$) in boiling THF was as facile as the reaction involving allyl bromide. The initial reaction mixture also had an IR spectrum similar to that of the allyl bromide reaction; however, we were unable to separate the products by chromatography, which prevented further characterization of the new compounds.

Discussion

Ligand substitution and oxidative addition reactions are well established for lower nuclearity clusters, especially with the iron triad elements which give stable and isolable products [21]. However, clean ligand substitution without disruption of the metal framework in higher nuclearity carbonyl clusters is much rarer [22]. Methods successfully employed to activate small clusters are not universally useful for their higher nuclearity counterparts [23]. Similarly, oxidative addition reactions involving high nuclearity metal clusters are also relatively rare, examples being the reaction of $[Rh_6(CO)_{15}]^{2-}$ with allyl bromide [19], reactions of $[Ru_6C(CO)_{16}]^{2-}$ with methyl iodide and allyl bromide [20], $Os_6(CO)_{16}(MeCN)_2$ with 1,5-COD [24], and the reactions of $Pt_2Os_4(CO)_{18}$ [25] and $Ru_6(CO)_{18}(\mu_4\text{-}S)$ [26] with dihydrogen.

Synthesis of mixed-metal clusters has allowed the examination of metal specificity in their reactions with organic molecules. Examples of small cluster systems showing metal specificity during ligand substitution have been described for various tri- and tetra-nuclear compounds [27–29], and an example of selective oxidative addition of dihydrogen at the ruthenium centers of $Ru_2Co_2(CO)_{13}$ has also been reported [30]. Studies of site selectivity have been extended to higher nuclearity mixed-metal clusters with a recent report of selective diphenylacetylene coordination in the compound $Pt_3Ru_6(CO)_{20}(\mu_3,\eta^2\text{-}C_2Ph_2)H_2$ [31].

In our earlier communication [6], the oxidative addition reactions of triphenylsilane and allyl bromide to the iridium(I) centers in $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ and $(\eta^5\text{-}C_9H_7)Ir(C_8H_{14})(CO)$ were found to take place under similar conditions. In contrast, the formally analogous cyclopentadienyl compound $(\eta^5\text{-}C_5H_5)Ir(C_8H_{14})(CO)$ did not undergo these reactions, even under more forcing conditions. Since the kinetics of the reaction of $(\eta^5\text{-}C_9H_7)Ir(C_8H_{14})(CO)$ with triphenylsilane indicate an *associative* reaction [32], presumably involving an η^5-to-η^3 'ring slip' of the indenyl ligand, a similar associative pathway, with an intermediate having a decreased number of Ir–Re interactions, may be involved in the reactions of $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$.

The pattern of reactivity between $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ and organic halides is not consistent with simple nucleophilic attack at carbon by the metal center [1]. In particular, the relatively facile reactions with allyl and propargyl bromide strongly suggest that coordination of the unsaturated groups precedes activation of the carbon–bromine bond. A feature that complicates these systems is that if some reaction does occur with $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$, the resulting halide ions, especially iodide, can react with the cluster framework in an unselective fashion, leading to the loss of one or more metal vertexes [33].

In summary, we have observed that the cluster anion $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ is a reactive species, with facile replacement of the cyclooctene ligand by stronger donors as well as by 'oxidative addends'. Further effort directed toward understanding the kinetics and mechanisms of these reactions as well as extension to other classes of reactants is highly warranted.

Acknowledgements

This work was supported by a grant from the National Science Foundation. L.Ma is grateful to the Department of Chemistry for fellowship support during the period 1988–1991.

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