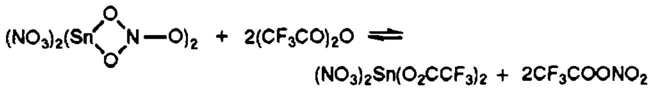
producing the trifluoroacetyl nitrate, i.e.



The formation of NO_2^+ and CF_3COO^- ions will be favored by the electron-withdrawing character of the CF_3 group; i.e., the following equilibrium will be shifted to the right:

$$CF_3COONO_2 \rightleftharpoons NO_2^+ + CF_3COO^-$$

This shift is more enhanced by the removal of trifluoroacetate ions through coordination to the metal ion, giving the complex (trifluoroacetato)metalate anion.

This is evident from the upfield shift of the ^{14}N NMR resonance; see Table I and Figure 2.

Registry No. $(NO_2)_2[Sn(O_2C_2F_3)_6]$, 68462-15-7; $CF_3C(O)ONO_2$, 66693-89-8; $NO_2^+CF_3COO^-$, 129176-51-8; $Sn(O_2C_2F_3)_4$, 16424-89-8; $Sn(NO_3)_4$, 13826-70-5; $(CF_3CO)_2O$, 407-25-0.

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Synthesis and Characterization of Heptarhenium Carbido Clusters with (η^2-Olefin)iridium Capping Moieties

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Studies of transition-metal η^2-olefin compounds have played very important roles in understanding the metal–ligand bonding as well as mechanisms of catalytic processes involved in alkene transformations.[1] Mononuclear η^2-olefin compounds with six-electron polyene auxillary ligands, such as cyclopentadienyl (Cp^-), benzene, and their derivatives, have received increased attention in that several late-transition-metal compounds have been established as useful C–H bond activation reagents.[2] Compared with mononuclear species, fewer polynuclear η^2-olefin compounds have been reported.[3] When alkenes are allowed to react with cluster compounds, facile C–H and/or C–C bond cleavage or formation is frequently encountered, preventing the isolation and characterization of η^2-olefin adducts.[4]

In a series of recent reports from our group and others, mixed-metal carbido cluster anions with the general formula of $[Re_7C(CO)_{21}ML_n]^{2-}$ have been synthesized by redox-coupling[5] of $[Re_7C(CO)_{21}]^{3-}$ and various ML_n^+ (M = Rh, Ir, Pt, Pd, Cu, Ag, Au) moieties.[6,7] An isolobal analogy between the Cp^- ligand and the anionic cluster compound $[Re_7C(CO)_{21}]^{3-}$ was proposed on the basis of the topological and expected frontier orbital similarities between them as well as the resemblance in the spectroscopic features of $[Re_7C(CO)_{21}ML_n]^{2-}$ and $CpML_n$.[6b] In terms of reactivity, metalloligand-supported metal centers also resemble their mononuclear analogues with respect to substitution reactions.[8] As part of our current attempt to extend the analogy between $[Re_7C(CO)_{21}]^{3-}$ and Cp^-, we report here the synthesis and characterization of the η^2-olefin-containing clusters $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ (C_8H_{14} = cyclooctene) and $[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]^{2-}$.

Experimental Section

General Procedures. All reactions were carried out under a nitrogen atmosphere by using standard Schlenk techniques and were monitored by IR spectroscopy (carbonyl region). Solvents were distilled from appropriate drying agents and degassed immediately before use. Cyclooctene (Aldrich) was purified by passing it through an aluminum oxide column and tested for the absence of peroxide with $FeSO_4$ and KSCN immediately before use. CP grade ethylene (Matheson) and $AgBF_4$ (Ozark-Mahoning) were used as received. $[PPN]_3[Re_7C(CO)_{21}]$ or $[Et_4N]_3[Re_7C(CO)_{21}]$[9] and $[Ir(C_8H_{14})_2(CO)Cl]_2$[10] were prepared according to literature methods. ^{13}CO-enriched $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ was prepared from ca. 20% ^{13}CO-enriched $[PPN]_3[Re_7C(CO)_{21}]$.

IR spectra were recorded with a Perkin-Elmer 1750 FT-IR spectrometer. ^1H NMR spectra were obtained by using a GE GN-500 spectrometer at 500 MHz. The ^{13}C NMR spectrum was acquired on a GE QE-300 instrument at 75 MHz. 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.

$[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$. THF solutions of $AgBF_4$ (9.6 mg, 0.049 mmol) and $[Ir(C_8H_{14})_2(CO)Cl]_2$ (30.1 mg, 0.0316 mmol) were combined, and cyclooctene (2.0 mL, 15 mmol) was added immediately after mixing. The solution became turbid after stirring at ambient temperature for 2 h. After the precipitate was allowed to settle, the yellow solution was transferred via a filtering cannula and passed through a layer of Celite on a fritted filter. This solution was mixed with a dichloromethane solution of $[PPN]_3[Re_7C(CO)_{21}]$ (83.7 mg, 0.0238 mmol), resulting in an immediate color change to dark red. After 30 min of stirring at room temperature, the solvents were removed under vacuum. The residue was dissolved in a minimal amount of chloroform, and 2-propanol was carefully layered on top. Solvent diffusion at room temperature for 12 days gave a black solid (70.2 mg). A recrystallization using chloroform/2-propanol was carried out over 5 days, giving dark red crystals (35.1 mg, 45%). Anal. Calcd for $C_{104}H_{75}N_2Cl_3IrO_{22}P_4Re_7$ ($[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]\cdot CHCl_3$): C, 36.41; H, 2.20; N, 0.82; Cl, 3.10. Found: C, 36.48; H, 2.12; N, 0.84; Cl, 2.89.[11] IR (acetone): ν_{CO} 2048 (w), 1996 (vs), 1973 (w), 1940 (w), 1921 (w), 1888 (vw) cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 7.80–7.40 (m, 60 H, C_6H_5 in PPN^+), 2.79 (m, 2 H, H_v), 2.16 (m, 2 H, $H_{\alpha 1}$), 1.72–1.50 (m, 10 H, $H_\beta + H_\gamma + H_{\alpha 2}$). ^{13}C NMR ($CDCl_3$, 20 °C): δ 204.7 (s, 3 C, $Re(CO)_3$ cap), 195.3 (s, 9 C), 191.2 (s, 9 C), 167.1 (s, 1 C, Ir–CO). FAB-MS (negative ion): m/z (^{187}Re, ^{193}Ir) 2778 (M – PPN), 2668 (M – PPN – C_8H_{14}), 2130 (M – 2PPN – C_8H_{14}).

$[PPN]_2[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]$. $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ (21.4 mg, 0.006 46 mmol) was dissolved in acetone (ca. 40 mL) in a 250-mL heavy-walled glass pressure bottle. The bottle was pressurized with ethylene (15 psig), (15 psi), and the solution was stirred at room temperature for 13 h. After the removal of the solvent, the residue

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(11) An analytically pure sample without solvent molecules was obtained as the Et_4N^+ salt $[Et_4N]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$. Anal. Calcd for $C_{47}H_{54}N_2IrO_{22}Re_7$: C, 22.63; H, 2.18; N, 1.12. Found: C, 22.39; H, 2.17; N, 1.10.

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Table I. Crystallographic Data for $[PPN]_2[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]$[13]

chem formula	$C_{97}H_{64}N_2O_{22}P_4Re_7$	fw	3229.1
a	13.663 (5) Å	space group (No.)	$P\bar{1}$ (No. 2)
b	15.401 (6) Å	T	26 °C
c	12.658 (4) Å	λ	0.71073 Å
α	96.18 (3)°	ρ_{calcd}	2.230 g cm^{-3}
β	107.83 (3)°	μ	104.03 cm^{-1}
γ	71.43 (3)°	transm coeff	0.224–0.723
V	2404 (2) Å^3	$R(F_o)^a$	0.066
Z	1	$R_w(F_o)^a$	0.071

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$; $w = k/([\sigma(R_o)]^2 + [pF_o]^2)$.

was dissolved in dichloromethane (2 mL), and 2-propanol was layered on top. After 2 days, solvent diffusion gave dark red crystals (9.2 mg, 44%). Anal. Calcd for $C_{97}H_{64}N_2IrO_{22}P_4Re_7$: C, 36.08; H, 2.00; N, 0.87. Found: C, 36.05; H, 2.01; N, 0.86. IR (acetone): ν_{CO} 2050 (w), 1997 (vs), 1941 (w), 1921 (w), 1894 (vw) cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 7.80–7.30 (m, 60 H, C_6H_5 in PPN$^+$), 3.38 (s, 4 H, C_2H_4). FAB-MS (negative ion): m/z (^{187}Re, ^{193}Ir) 2696 (M – PPN), 2668 (M – PPN – CO or C_2H_4), 2158 (M – 2PPN), 2130 (M – 2PPN – CO or C_2H_4).

Crystallographic Study. Dark red crystals of $[PPN]_2[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]$ suitable for X-ray crystallographic study were grown from dichloromethane/2-propanol solvent layers at room temperature over 2 days. A crystal with the dimensions of 0.03 × 0.1 × 0.4 mm was mounted onto a thin glass fiber with epoxy, and data were collected with a Syntex P2$_1$ automated four-circle diffractometer. Unit cell parameters were obtained by a least-squares fit of 15 machine-centered reflections (17.2° $\leq 2\theta \leq$ 18.0°). A total of 6444 independent reflections (R_i = 0.026) in the range of 3.0° $\leq 2\theta \leq$ 46.0°, among which were 2774 observed reflections ($I > 2.58\sigma(I)$), were collected by scanning $\pm h,\pm k,\pm l$ at a variable scan rate over 91.5 h with no change in the appearance of the crystal. Absorption, Lorentz, polarization, and anomalous dispersion corrections were applied to the reflection intensities.

The positions of the metal atoms were located from an E map by using direct methods (SHELXS-86).[12] Subsequent least-squares difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms in the ethylene ligand were not located on the electron density maps. The PPN$^+$ phenyl rings with hydrogen atoms were treated as idealized contributors, and Re–C(carbide) bond lengths were restrained to one variable parameter as was the Ir–C14(carbonyl) distance. Anisotropic thermal coefficients were refined for the octahedral framework rhenium atoms (Re2–Re4); four sets of group isotropic thermal parameters were refined for the capping metal (Ir and Re1), carbon (C11–C14), oxygen (O11-O14), and the PPN$^+$ hydrogen atoms, respectively. Isotropic coefficients were refined for the remaining non-hydrogen atoms. A maximum shift/error of 0.061 in the last cycle indicated successful convergence. The highest peaks in the final difference Fourier map (+2.71 > e/Å^3 > –1.54) were in the vicinity of the metal atoms. A final analysis of variance between observed and calculated structure factors showed no significant systematic errors. Selected crystallographical data are listed in Table I.[13]

Results

The mixed-metal carbonyl cluster compound $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ was synthesized via a capping reaction of $[PPN]_3[Re_7C(CO)_{21}]$ by the cationic species derived from $[Ir(C_8H_{14})_2(CO)Cl]_2$. Substitution of the cyclooctene ligand in $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ by ethylene gave $[PPN]_2[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]$. IR, ^1H and ^{13}C NMR, and FAB-MS studies and an X-ray crystal analysis of $[PPN]_2[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]$ were undertaken, whose results are presented in the Experimental Section as well as in the sections that follow.

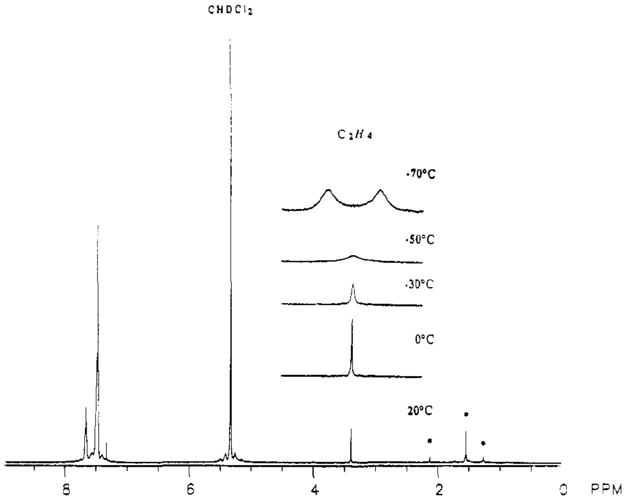

Figure 1. Variable-temperature ^1H NMR (CD_2Dl_2) spectra of $[PPN]_2[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]$. Inserts show expanded ethylene resonances at different temperatures. Asterisks indicate impurities due to residual acetone, H_2O, and 2-propanol.

Discussion

Synthesis. In the continuation of our systematic syntheses of high-nuclearity mixed-metal clusters,[6] $[Re_7C(CO)_{21}]^{3-}$ was directly treated with $[Ir(C_8H_{14})_2(CO)Cl]_2$. However, a slow and complex reaction at ambient temperature prevented the isolation of a single product. Our previous experiments have shown that monovalent cationic species generated from the reactions between transition-metal dimers and $AgBF_4$ readily react with $[Re_7C(CO)_{21}]^{3-}$.[6b] In order to increase the reaction rate and reduce complications, the same procedure was adopted for our current synthesis. Although no attempt was made to isolate and identify a cationic species from the reaction between $[Ir(C_8H_{14})_2(CO)Cl]_2$ and $AgBF_4$, its existence was suggested by the formation of a AgCl precipitate. After the removal of the precipitate, solution of the "cationic" species was subsequently added to a solution containing $[Re_7C(CO)_{21}]^{3-}$ and clean formation of $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ was observed.

The suggested cationic iridium fragment from chloride abstraction is formally four electrons deficient in comparison with the iridium center of $[Ir(C_8H_{14})_2(CO)Cl]_2$, which has an eighteen valence electron configuration. However, the capping principle developed by Mingos[14] requires a twelve-electron transition-metal fragment to cap a triangular face in deltahedron clusters, such as $[Re_7C(CO)_{21}]^{3-}$. Therefore, dissociation of another two-electron ligand from the iridium center is necessary to form the proper capping fragment. The formation of $[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]^{2-}$ suggests that the cyclooctene ligands are weakly bound compared to the carbonyl ligand and a preferential dissociation of a cyclooctene ligand occurred in the overall capping reaction.

The cyclooctene ligand in the mixed-metal cluster $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ is also reactive, similar to its labile nature in $[Ir(C_8H_{14})_2(CO)Cl]_2$.[10] Clean substitution of cyclooctene by ethylene readily occurred at moderate pressure (15 psig) and room temperature in a period of 10–15 h to form another η^2-olefin cluster compound $[PPN]_2[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]$.

Spectroscopic Characterization. $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ and $[PPN]_2[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]$ both have IR (carbonyl region) patterns characteristic of other $[Re_7C(CO)_{21}ML_n]^{2-}$ compounds.[6] Minor spectral differences (1–2 cm^{-1}) between them indicate the similarity in the combined donor/acceptor ability of cyclooctene and ethylene. Unlike the IR spectra of $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ and $[Re_7C(CO)_{21}Rh(CO)(PPh_3)]^{2-}$,[6b] a separate band for the iridium-bound carbonyl group was not observed, probably due to coincidental degeneracy with the broad strong band. Assuming the iridium-bound carbonyl of $[PPN]_2[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]$ is in the same region as the strong

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(12) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M.; Kruger, C.; Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175–189.

(13) We would like to acknowledge the suggestion by a reviewer who kindly pointed out our unconventional setting for a reduced cell listed in Table I. Transformation to the conventional setting, a^* = 12.658 (4) Å, b^* = 13.663 (5) Å, c^* = 15.401 (6) Å, α^* = 71.43 (3)°, β^* = 83.82 (3)°, γ^* = 72.17 (3)°, is accomplished by using the matrix

$$\begin{pmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix}$$

The atomic coordinates in Table II are also given under the nonstandard setting.

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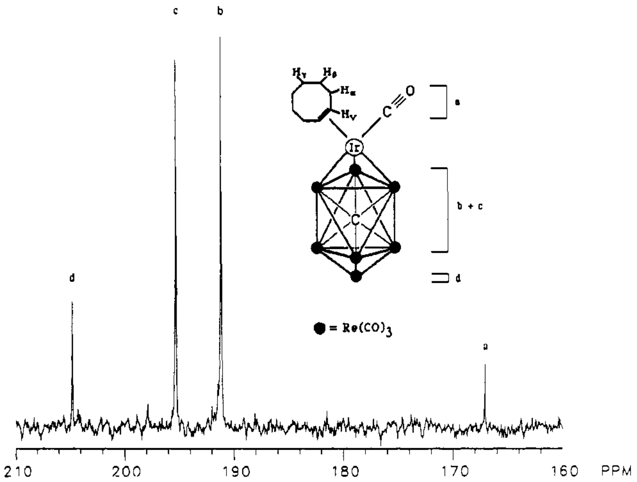

Figure 2. ^{13}C NMR (CDCl$_3$, 20 °C) spectrum (carbonyl region) of [PPN]$_2$[Re$_7$C(CO)$_{21}$Ir(C$_8$H$_{14}$)(CO)].

band (1997 ± 10 cm^{-1}), comparison with that of the cyclopentadienyl analogue CpIr(C$_2$H$_4$)(CO) (1980 cm^{-1})[15] provides a good agreement with our previous conclusion that [Re$_7$C(CO)$_{21}$]$^{3-}$ is a weaker electron donor than the Cp$^-$ ligand.[6b]

The ^{1}H NMR spectrum of [PPN]$_2$[Re$_7$C(CO)$_{21}$Ir(C$_8$H$_{14}$)(CO)] has a complex pattern for the cyclooctene ligand. Assignments of the vinyl hydrogen (H$_v$) and part of the α hydrogens (H$_\alpha$) resonances were made from results of homonuclear decoupling experiments by irradiating these resonances. The vinyl hydrogen signal was observed as a multiplet centered at 2.79 ppm with a large coupling of 11.5 Hz. Integration showed that only half of the four α hydrogens (H$_{\alpha1}$) resonate at 2.16 ppm showing the 11.5-Hz coupling. The signal of the other half (H$_{\alpha2}$) overlaps with the β and γ hydrogen (H$_\beta$, H$_\gamma$) signals, and together they appear as two sets of multiplets in the region between 1.72 and 1.50 ppm. The difference in the chemical environment among the α hydrogens may be attributed to the difference in their orientations relative to the basal trirhenium plane (endo and exo).

For [PPN]$_2$[Re$_7$C(CO)$_{21}$Ir(C$_2$H$_4$)CO)], a single signal for the coordinated ethylene ligand was located at 3.38 ppm at 20 °C. The inner and outer sets of two hydrogen atoms relative to the iridium-bound carbonyl ligand became equivalent under the condition due to a fast rotation process of the ethylene ligand around the coordination vector (vide infra).

Dynamic Processes in Solution. A variable-temperature ^{1}H NMR study of [PPN]$_2$[Re$_7$C(CO)$_{21}$Ir(C$_2$H$_4$)(CO)] revealed a rotation process of the ethylene ligand, as frequently observed for mononuclear η^2-ethylene complexes.[16] ^{1}H NMR spectra at temperatures from 20 to −70 °C are shown in Figure 1. At −70 °C, two resonances at 3.56 and 3.19 ppm were observed for the inner and outer hydrogens. At temperatures above −50 °C, only a single resonance at 3.38 ppm was observed. The approximate coalescence temperature for the ethylene rotation process is −60 ± 10 °C, from which the estimated $\Delta G^\ddagger$ of the rotation is ~9.8 ± 0.5 kcal/mol. This value is lower than reported for CpIr(C$_2$H$_4$)(CO) (~20.0 ± 0.2 kcal/mol) and (η^5-C$_9$H$_7$)Ir(C$_2$H$_4$)(CO) (~13.9 ± 0.2 kcal/mol).[15] We cannot conclude the lower value is simply due to a ground-state effect, i.e., the difference in electron-donating ability between [Re$_7$C(CO)$_{21}$]$^{3-}$ and Cp$^-$, as the possibility exists for a transition-state effect, which allows the iridium cap to slip to lower the energy barrier for the ethylene rotation. This would however confirm [Re$_7$C(CO)$_{21}$]$^{3-}$ being a weaker electron donor than a cyclopentadienyl ligand and/or an indenyl ligand.

In the ^{13}C NMR spectrum of [PPN]$_2$[Re$_7$C(CO)$_{21}$Ir(C$_8$H$_{14}$)(CO)], which was obtained by reacting ^{13}CO-enriched [PPN]$_3$[Re$_7$C(^{13}CO)$_{21}$] with nonenriched [Ir(C$_8$H$_{14}$)$_2$(CO)Cl]$_2$, a 3:9:9 pattern between 204.7 and 191.2 ppm and a signal of relative intensity of 1 at 167.1 ppm were observed (shown in Figure 2). By comparison with other [Re$_7$C(CO)$_{21}$ML$_n$]$^{2-}$ compounds, the three lower field resonances were attributed to the 21 rhenium-bound carbonyls. The 3:9:9 ratio also indicates that the mixed-metal cluster has a 1,4-bicapped octahedral geometry.[6b] The higher field signal was assigned to the iridium-bound carbonyl ligand on the basis of its relative intensity. The intensity of this signal with respect to other rhenium carbonyl resonances suggests the occurrence of carbonyl scrambling from rhenium to iridium in this compound. The chemical shift of this iridium-bound carbonyl is similar to those observed in the cyclopentadienyl (two isomers, δ 170.0 and 171.2) and indenyl (also two isomers, δ 168.6 and 170.3) analogues.[15]

Table II. Selected Fractional Coordinates for [Re$_7$C(CO)$_{21}$Ir(C$_2$H$_4$)(CO)]$^{2-}$

	x/a	y/b	z/c
Ir	0.2589 (7)	0.4940 (5)	−0.0037 (6)
Re1	0.2755 (7)	0.4831 (5)	0.0120 (6)
Re2	0.0949 (2)	0.5755 (1)	0.1113 (1)
Re3	0.0432 (2)	0.5346 (1)	−0.1233 (1)
Re4	0.1350 (2)	0.3808 (1)	0.0277 (1)
O11	0.459 (5)	0.423 (4)	0.205 (5)
O12	0.335 (4)	0.648 (4)	−0.035 (4)
O13	0.427 (4)	0.362 (4)	−0.116 (4)
O14	0.463 (5)	0.450 (4)	0.186 (5)
O21	0.289 (2)	0.513 (2)	0.314 (2)
O22	−0.006 (3)	0.705 (2)	0.279 (2)
O23	0.167 (2)	0.740 (2)	0.079 (2)
O31	−0.127 (2)	0.578 (2)	−0.355 (2)
O32	0.087 (3)	0.711 (2)	−0.167 (3)
O33	0.181 (2)	0.423 (2)	−0.283 (2)
O41	0.101 (3)	0.199 (3)	0.055 (3)
O42	0.319 (3)	0.315 (2)	0.236 (3)
O43	0.277 (3)	0.260 (2)	−0.109 (3)
C	0.0000	0.5000	0.0000
C11	0.412 (3)	0.451 (5)	0.117 (5)
C12	0.306 (5)	0.590 (3)	−0.006 (5)
C13	0.374 (4)	0.401 (4)	−0.055 (5)
C14	0.384 (4)	0.471 (5)	0.117 (4)
C21	0.213 (2)	0.534 (2)	0.237 (2)
C22	0.024 (3)	0.652 (2)	0.209 (3)
C23	0.140 (2)	0.673 (1)	0.089 (2)
C31	−0.061 (3)	0.561 (3)	−0.271 (2)
C32	0.071 (3)	0.643 (1)	−0.152 (3)
C33	0.140 (3)	0.467 (3)	−0.210 (3)
C41	0.117 (4)	0.265 (2)	0.028 (4)
C42	0.245 (2)	0.345 (2)	0.161 (2)
C43	0.240 (4)	0.321 (5)	−0.044 (5)
C1	0.368 (5)	0.462 (5)	−0.090 (5)
C2	0.341 (6)	0.574 (5)	−0.048 (6)

Table III. Selected Bond Distances (Å) and Angles (deg) for [PPN]$_2$[Re$_7$C(CO)$_{21}$Ir(C$_2$H$_4$)(CO)]

	(a) Distances		
Re1–Re2	2.995 (8)	Re2–C	2.123 (2)
Re1–Re3	3.032 (9)	Re3–C	2.104 (2)
Re1–Re4	2.904 (8)	Re4–C	2.117 (2)
Re2–Re3	2.988 (2)	Ir–Re2′	2.921 (8)
Re2–Re4	3.005 (2)	Ir–Re3′	2.798 (8)
Re2–Re3′	2.990 (2)	Ir–Re4′	2.917 (8)
Re2–Re4′	2.990 (3)	Ir–C14	1.88 (5)
Re3–Re4	2.977 (2)	Ir–C$_2$H$_4$	1.89 (6)
Re3–Re4′	2.992 (3)		
	(b) Angles		
Re2′–Ir–Re3′	62.9 (2)	Re2′–Ir–Re4′	62.0 (2)
Re3′–Ir–Re4′	62.7 (2)	OC–Ir–C$_2$H$_4$	80 (3)

Solid-State Structure of [PPN]$_2$[Re$_7$C(CO)$_{21}$Ir(C$_2$H$_4$)(CO)]. [PPN]$_2$[Re$_7$C(CO)$_{21}$Ir(C$_2$H$_4$)(CO)] crystallizes in the triclinic $P\bar{1}$ space group. Each unit cell contains one molecule, which resides at the inversion center, imposing a crystallographic C_i symmetry. Since the molecule has a 1,4-bicapped octahedral structure (vide infra), a 2-fold "end-to-end" disorder problem was encountered in the structural determination, which caused the

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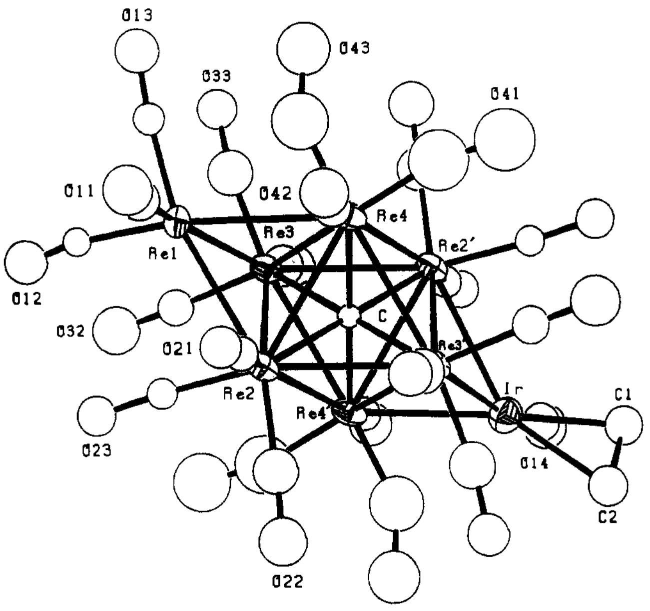

Figure 3. ORTEP diagram of the anion [Re$_7$C(CO)$_{21}$Ir(C$_2$H$_4$)(CO)]$^{2-}$ showing 35% probability ellipsoids.

superposition of the Re(CO)$_3$ and Ir(C$_2$H$_4$)(CO) capping moieties. Although the positions of rhenium and iridium atoms of the capping groups were successfully separated and refined without resorting to the half-occupancy method, this 2-fold disorder still made three out of the six octahedron skeletal rhenium atoms (Re2', Re3', Re4') crystallographically indistinguishable from their center of symmetry related counterparts. In Tables II and III, only the unique atomic positions, six of twelve skeletal Re–Re bonds, and three Re–C(carbide) distances are listed. Due to the disorder problem, the determined C–C distance for the ethylene ligand is 1.7 (1) Å, considerably longer than C–C distances in transition-metal η^2-ethylene systems.[1a]

The ORTEP drawing of the [Re$_7$C(CO)$_{21}$Ir(C$_2$H$_4$)(CO)]$^{2-}$ anion in Figure 3 shows that it adopts a 1,4-bicapped octahedral geometry as observed for other compounds dervied from [Re$_7$C(CO)$_{21}$]$^{3-}$.[6,7,17] The octahedral framework Re–Re bonds are quite uniform, varying from 2.977 (2) to 3.005 (2) Å with the average Re–Re distance being 2.990 (3) Å. This value is in good agreement with those observed for [Re$_7$C(CO)$_{21}$Au(PPh$_3$)]$^{2-}$ (3.011 (1) Å),[6a] [Re$_7$C(CO)$_{21}$Pt(C$_4$H$_7$)]$^{2-}$ (2.999 (2) Å),[6b] [Re$_7$C(CO)$_{21}$Pd(C$_9$H$_9$)]$^{2-}$ (2.998 (2) Å),[6c] [Re$_7$C(CO)$_{21}$Ag]$^{2-}$ of [{Re$_7$C(CO)$_{21}$}$_2$Ag]$^{5-}$ (3.008 (3) Å),[7], and [Re$_8$C(CO)$_{24}$]$^{2-}$ (2.993 (1) Å).[17] The average Re–C(carbide) distance of 2.115 (2) Å is also similar to those in the aforementioned compounds (2.116 (1)–2.13 (3) Å). The iridium capping moiety is bonded to the rhenium triangle rather symmetrically in comparison to other capped heptarhenium clusters,[6b,c,7] with the Ir–Re distances varying from 2.904 (8) to 3.032 (9) Å. This could be attributed to the steric similarity of an ethylene ligand and a carbonyl ligand. The coordination geometry around the capping iridium is that of a pseudo trigonal bipyramid. The C–C axis of the ethylene ligand is almost parallel to the equatorial plane formed by Re2', Re4', and the center of the ethylene, which is the most favored geometry predicted for mononuclear five-coordinate complexes containing ethylene ligands.[18] The iridium–ethylene distance is 1.89 (6) Å, which is shorter than the metal–ethylene distances in most other mononuclear[1a] and cluster compounds[2b,f] (2.0–2.3 Å). However, limitations of the crystal structure prevent further comparisons.

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Supplementary Material Available: For [PPN]$_2$[Re$_7$C(CO)$_{21}$Ir(C$_2$H$_4$)(CO)], tables of atomic coordinates, thermal parameters, and complete bond distances and angles and a unit cell packing diagram (12 pages); a table of final observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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