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SYNTHESIS, STEREODYNAMICS, AND REACTIVITY OF ISONITRILE DERIVATIVES OF DODECACARBONYLTETRAIRIDIUM *

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Summary

The reaction of $Ir_4(CO)_{12}$ with t-BuNC or MeNC in the presence of trimethylamine oxide in refluxing tetrahydrofuran provides the substituted iridium clusters $Ir_4(CO)_{12-x}(RNC)_x$ (x = 1—4; R = t-Bu, Me). The infrared and ^{13}C NMR spectra of these molecules indicate that most of them adopt structures related to $Ir_4(CO)_{12}$, i.e., they have only terminal carbonyl ligands. The variable temperature ^{13}C NMR spectra for $Ir_4(CO)_{11}$(t-BuNC) establish a carbonyl scrambling process which is the formal inverse of the $C_{3v} \rightarrow T_d$ scrambling mechanism proposed for $Rh_4(CO)_{12}$. The kinetics of substitution of $Ir_4(CO)_{12}$ by t-BuNC have been studied. Each substitution step occurs by a ligand-dependent, overall second-order reaction at a rate much greater than for substitution by PPh_3. The observed differences between t-BuNC and PPh_3 can be rationalized on the basis of steric differences between the two ligands.

Introduction

Studies on the cobalt triad compounds $M_4(CO)_{12}$ (M = Co, Rh, Ir) and their derivatives have raised a number of important questions regarding structure, fluxionality, and reactivity in metal cluster chemistry. For the compounds $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, and their simple substitution derivatives a carbonyl-bridged, "C_{3v}-like" structure (1) is adopted [1,2]. The mixed metal clusters $M_{4-x}M'_x(CO)_{12}$ (M, M' = Co, Rh, Ir) adopt analogous carbonyl-bridged structures [3]. In contrast $Ir_4(CO)_{12}$ adopts a structure 2 with only terminal carbonyl ligands and idealized T_d symmetry [4]. However, upon substitution of one or more carbonyl ligands by a phosphorus [5] or arsenic [6] ligand, 1,5-cyclooctadiene [7], or various anions [8] a C_{3v}-like, carbonyl-bridged structure is adopted.

There are a number of reports concerning carbonyl mobility in $M_4(CO)_{12}$

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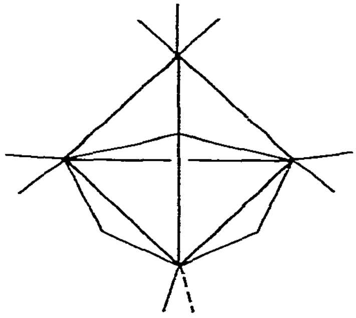
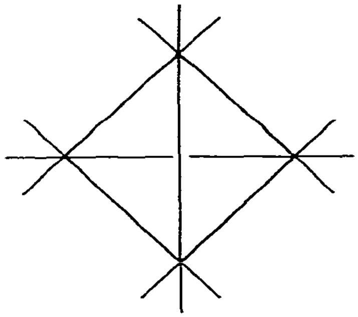
* Dedicated to the memory of Paolo Chini.



(1)



(2)

(M = Co, Rh, Ir) and their derivatives [9]. Cotton first proposed that scrambling of all twelve carbonyl ligands in $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ might occur by means of rapid interconversions between carbonyl-bridged (1) and unbridged (2) forms [10]. Complete carbonyl site exchange has been established for $Rh_4(CO)_{12}$ [11], and the mechanism proposed by Cotton has been invoked to explain the results. The variable temperature ^{13}C NMR spectra obtained for $Ir_4(CO)_{11}(PPh_2Me)$ were later shown to be consistent with the operation of this mechanism at low temperatures [5a]. However, variable temperature ^{13}C NMR spectral data reported for the structurally related $RhCo_3(CO)_{12}$ are incompatible with the intermediacy of 2 in the lowest energy carbonyl scrambling process [12]. Alternative mechanisms have been presented and discussed [9]. Similarly, $Ir_4(CO)_{10}$(diars) [6] and $Rh_4(CO)_8[P(OPh)_3]_4$ [2b] display ^{13}C NMR spectra which indicate the operation of other low energy carbonyl scrambling processes.

Only two investigations of carbonyl ligand-substitution kinetics for $M_4(CO)_{12}$ and related compounds have been published. Karel and Norton [13] examined the substitution of $Ir_4(CO)_{12}$ by PPh_3 and found that, whereas the first substitution proceeds by a $[PPh_3]$-dependent mechanism, the later steps proceed by faster, $[PPh_3]$-independent, carbonyl-dissociation pathways. Similarly, a recent study [14] of the substitution of $Co_4(CO)_{12-x}[P(OMe)_3]_x$ (x = 1, 2) by $P(OMe)_3$ showed that the rate of reaction with $Co_4(CO)_{11}P(OMe)_3$ is strongly dependent on the concentration of $P(OMe)_3$ but the rate with $Co_4(CO)_{10}[P(OMe)_3]_2$ is not.

We report here the synthesis and characterization of two series of isonitrile derivatives of $Ir_4(CO)_{12}$, namely, $Ir_4(CO)_{12-x}L_x$ (x = 1—4, L = t-BuNC, MeNC). These derivatives have been found to adopt primarily unbridged structures [15]. Carbonyl scrambling in $Ir_4(CO)_{11}$(t-BuNC) has been studied in detail by ^{13}C NMR and kinetic data for the substitution of $Ir_4(CO)_{12-x}(t\text{-}BuNC)_x$ (x = 0—3) by t-BuNC have been obtained.

Experimental section

Chemicals

Reagent grade solvents were obtained from standard commercial sources and generally were used without further purification. Methylisonitrile [16] and t-butylisonitrile [17] were prepared according to published procedures. Trimethylamine oxide dihydrate ($Me_3NO \cdot 2\ H_2O$) was purchased from Aldrich Chemical Co. and used as received. Iridium trichloride trihydrate was obtained from Engelhard Industries. Tetrairidiumdodecacarbonyl was prepared as previously described [18]. Separations were generally performed by preparative-scale thin layer chromatography. TLC plates were prepared from Silica Gel G (type 60, Merck) with a thickness of ca. 1 mm. Microanalyses were performed by the University of Illinois analytical laboratory under the direction of Mr. Joseph Nemeth. Infrared spectra were recorded on a Perkin Elmer 521 spectrometer and the peaks were calibrated against the 2138.5 cm^{-1} peak of cyclohexane and the 1601.4 cm^{-1} peak of polystyrene. ^1H NMR spectra were recorded on a Varian HA-100 spectrometer. Chemical shifts were measured against internal TMS. ^{13}C NMR spectra were recorded on either a Varian XL-100 spectrometer operating at 25.2 MHz or a JEOL-FX-60 spectrometer at 15.03 MHz. Samples were enriched with ^{13}CO to levels of 30—70% as judged by mass spectrometry. $Cr(acac)_3$ (ca. 0.03 *M*) was added as a relaxation agent for the carbonyls. Chemical shifts were determined relative to internal TMS. Temperatures were measured by means of a copper-constantan thermocouple. Mass spectra were obtained in the electron impact mode (70 eV) on a Varian MAT CH-5 mass spectrometer by Mr. Joe Wrona.

$Ir_4(CO)_{11}(t\text{-}BuNC)$ and $Ir_4(CO)_{10}(t\text{-}BuNC)_2$

A solution of chlorobenzene (700 ml) and $Ir_4(CO)_{12}$ (606 mg, 0.549 mmol) was heated to reflux under nitrogen. To this refluxing solution was added a solution of t-BuNC (10 μl) and chlorobenzene (20 ml). After five minutes the solution was removed from the oil bath and allowed to cool. The solvent was removed and the yellow residue extracted with dichloromethane (5 ml). This solution was concentrated and the products purified by preparative-scale TLC (pentane) affording $Ir_4(CO)_{11}$(t-BuNC) (20 mg) and $Ir_4(CO)_{10}$(t-BuNC)$_2$ (7 mg) as yellow solids. The yields were 18% and 6%, respectively, based on added t-BuNC. The unreacted $Ir_4(CO)_{12}$ was easily recovered as a yellow powder after the extraction of the products with dichloromethane.

$Ir_4(CO)_{11}$(t-BuNC). IR (ν(CO), cyclohexane, cm^{-1}) 2094m, 2057vs, 2038s, 2016s, 2008m, ν(CN): 2181m; MS (*m/e*, ^{193}Ir) 1163 (M^+); ^1H NMR ($CDCl_3$, τ) 8.62.

Anal. Found: C, 16.63; H, 0.83; N, 1.16. Calcd. for $C_{16}H_9O_{11}NIr_4$: C, 16.56, H, 0.78; N, 1.21%.

$Ir_4(CO)_{10}$(t-BuNC)$_2$. Ir (ν(CO), cyclohexane, cm^{-1}) 2073m, 2042vs, 2031s, 2025s, 2018(sh), 1996m, 1982w, 1973w, 1966vw, ν(CN): 2164m; MS (*m/e*, ^{193}Ir) 1218 (M^+); ^1H NMR ($CDCl_3$, τ) 8.64.

Anal. Found: C, 20.15; H, 1.64; N, 2.25. Calcd. for $C_{20}H_{18}O_{10}N_2Ir_4$: C, 19.77; H, 1.49; N, 2.31%.

These compounds were also conveniently prepared utilizing $Me_3NO \cdot 2\ H_2O$. Solid $Ir_4(CO)_{12}$ (55 mg, 0.05 mmol) was dissolved in refluxing tetrahydrofuran (250 ml) under nitrogen. To this solution was added a solution of acetonitrile (20 ml) and $Me_3NO \cdot 2\ H_2O$ (5.5 mg, 0.05 mmol). The solution was heated at reflux for ten min. To this yellow solution t-BuNC (20 μl) was added. The solution was allowed to cool and the solvent removed at reduced pressure. Purification of the products by preparative-scale TLC (pentane) gave $Ir_4(CO)_{11}$(t-BuNC) (4 mg, 7%), $Ir_4(CO)_{10}$(t-BuNC)$_2$ (16 mg, 27%), and $Ir_4(CO)_9$(t-BuNC)$_3$ (4 mg, 6%).

$Ir_4(CO)_9$(t-BuCNC)$_3$

Solid $Ir_4(CO)_{12}$ (50 mg, 0.045 mmol) was dissolved in refluxing tetrahydrofuran (250 ml). To this solution was added t-BuNC (100 μl) quickly followed by $Me_3NO \cdot 2\ H_2O$ (5 mg, 0.045 mmol) in tetrahydrofuran (20 ml). The solution was heated at reflux for five min, and then allowed to cool. After removal of the solvent, the yellow oil was purified by preparative-scale TLC affording yellow $Ir_4(CO)_{10}$(t-BuNC)$_2$ (3 mg, 5%) and yellow $Ir_4(CO)_9$(t-BuNC)$_3$ (43 mg, 74%).

$Ir_4(CO)_9$(t-BuNC)$_3$. IR (ν(CO), cyclohexane, cm^{-1}) 2050m, 2028vs, 2010s(br), 1985s, 1981s, 1966w, 1952vw, 1835w, 1823w, ν(CN): 2153s; MS (m/e, ^{193}Ir) 1273 (M^+); ^{1}H NMR ($CDCl_3$, τ) 8.65.

$Ir_4(CO)_8$(t-BuNC)$_4$

To a refluxing solution of tetrahydrofuran (300 ml) and $Ir_4(CO)_{12}$ (86 mg, 0.078 mmol) was added t-BuNC (150 μl) followed immediately by solid $Me_3NO \cdot 2\ H_2O$ (32.5 mg, 0.293 mmol). Heating was continued for five min. After cooling, the solvent was removed and the products purified by preparative-scale TLC (pentane/dichloromethane, 1/1). This provided $Ir_4(CO)_8$-(t-BuNC)$_4$ (62 mg, 60%) as a yellow solid.

$Ir_4(CO)_8$(t-BuNC)$_4$. IR (ν(CO), cyclohexane, cm^{-1}) 2030m, 1999s, 1991sh, 1978m, 1968m, 1820m, 1810m, ν(CN): 2148s; MS (m/e, ^{193}Ir) 1323 (M^+); ^{1}H NMR ($CDCl_3$, τ) 8.56.

$Ir_4(CO)_{11}$(MeNC) and $Ir_4(CO)_{10}$(MeNC)$_2$

Solid $Ir_4(CO)_{12}$ (665 mg, 0.602 mmol) was dissolved in refluxing tetrahydrofuran (600 ml). To this solution was added MeNC (5.0 μl, 0.122 mmol). The solution was heated at reflux for five min, and then allowed to cool at room temperature. The solvent was removed and the dichloromethane (20 ml) soluble products purified by preparative-scale TLC (pentane). This provided $Ir_4(CO)_{11}$(MeNC) (60 mg, 44%) and $Ir_4(CO)_{10}$(MeNC)$_2$ (20 mg, 15%). The unreacted $Ir_4(CO)_{12}$ was recovered as a yellow powder after extraction of the dichloromethane-soluble products.

$Ir_4(CO)_{11}$(MeNC). IR (ν(CO), cyclohexane, cm^{-1}) 2095m, 2056vs, 2039s, 2016s, 2006m, 1998w, ν(CN): 2204m; MS (m/e, ^{193}Ir) 1121 (M^+); ^{1}H NMR ($CDCl_3$, τ) 6.24.

Anal. Found: C, 14.08; H, 0.45; N, 1.6. Calcd. for $C_{13}H_3O_{11}NIr_4$: C, 13.97; H, 0.27; N, 1.25%.

$Ir_4(CO)_{10}$(MeNC)$_2$. IR (ν(CO), cyclohexane, cm^{-1}) 2076m, 2045vs, 2031s, 2025s, 2018(sh), 2004w, 1994m, 1938w, 1974w, ν(CN): 2194m; MS (m/e, ^{193}Ir) 1134 (M^+); ^{1}H NMR ($CDCl_3$, τ) 6.33.

Anal. Found: C, 14.89; H, 0.67; N, 2.36. Calcd. for $C_{14}H_6O_{10}N_2Ir_4$: C, 14.87; H, 0.53; N, 2.48%.

$Ir_4(CO)_9$(MeNC)$_3$ and $Ir_4(CO)_8$(MeNC)$_4$

Solid $Ir_4(CO)_{12}$ (84 mg, 0.076 mmol) was added to tetrahydrofuran (300 ml) at reflux under nitrogen. To this solution was added MeNC (30 μl) followed immediately by $Me_3NO \cdot 2\ H_2O$ (34 mg, 0.306 mmol). The solution was heated at reflux for five min, allowed to cool, and the solvent removed at reduced pressure. The yellow oil was purified by preparative-scale TLC (pentane/dichloromethane, 1/1) yielding $Ir_4(CO)_9(MeNC)_3$ (20 mg, 30%) and $Ir_4(CO)_8(MeNC)_4$ (43 mg, 49%) as yellow solids.

$Ir_4(CO)_9(MeNC)_3$. IR (ν(CO), cyclohexane, cm^{-1}) 2062(sh), 2055m, 2032vs, 2019s, 2013s, 3008(sh), 1982s, 1965w, 1952w, ν(CN): 2184s; MS (*m/e*, ^{193}Ir) 1147 (M^+); ^{1}H NMR ($CDCl_3$, τ) 6.37.

Anal. Found: C, 15.86; H, 0.79; N, 3.58. Calcd. for $C_{15}H_9O_9N_3Ir_4$: C, 15.75; H, 0.79; N, 3.67%.

$Ir_4(CO)_8(MeNC)_4$. IR (ν(CO), cyclohexane, cm^{-1}) 2033m, 2014m, 2001vs, 1994s, 1977s, 1967s, 19542, 1943w, ν(CN): 2175s, 2155(sh); MS (*m/e*, ^{193}Ir) 1160 (M^+); ^{1}H NMR ($CDCl_3$, τ) 6.39.

Anal. Found: C, 16.39; H, 1.28; N, 4.57. Calcd. for $C_{16}H_{12}O_8N_4Ir_4$: C, 16.61; H, 1.05; N, 4.84%.

$Ir_4(CO)_{10}(PPh_3)$(t-BuNC)

A benzene solution (25 ml) of $Ir_4(CO)_{11}(PPh_3)$ (28 mg, 0.021 mmol) and t-BuNC (1.7 μl, 0.021 mmol) was heated at 60°C for 1.5 h. The solvent was then removed at reduced pressure and the yellow-orange oil purified by preparative-scale TLC (pentane/dichloromethane, 1/1) affording $Ir_4(CO)_{11}(PPh_3)$ (8 mg) and orange $Ir_4(CO)_{10}(PPh_3)$(t-BuNC) (12 mg, 41%).

$Ir_4(CO)_{10}(PPh_3)$(t-BuNC). IR (ν(CO), cyclohexane, cm^{-1}) 2068s, 2042vs, 2031s, 2008s(br), 1989w, 1840m, 1819m, ν(CN): 2171m; MS (*m/e*, ^{193}Ir) 1397 (M^+).

Kinetics of substitution by t-BuNC

Due to the limited solubility of $Ir_4(CO)_{12}$ in chlorobenzene at ambient temperatures, a matched pair of solution cells with long pathlengths were constructed. Two NaCl plates were clamped together using a 1.6 mm teflon washer as a spacer and sealed around the outer edges with epoxy cement. A small slice cut out of the spacer at the top of the cell allowed easy loading of the cells. The reactions were carried out in freshly distilled chlorobenzene under nitrogen in a water bath which was maintained at constant temperature (±0.3°C) by a thermistor. For reactions at temperatures above 28.3°C, aliquots of the reaction solution were removed and quenched at 0°C. After quenching, each aliquot was loaded into the IR cell and the absorbance of a strong, isolated carbonyl stretching frequency was measured immediately. This measurement required less than 15 seconds. For the reactions at 28.3°C, the aliquots were loaded directly into the cell and the time measured when the carbonyl stretching frequency was recorded. The room temperature during this process was 27 ± 2°C. The following absorptions were monitored due to their strong absorbance and isolation from other absorptions in both the starting material and products: $Ir_4(CO)_{12}$, 2070 cm^{-1}; $Ir_4(CO)_{11}(PPh_3)$, 2054 cm^{-1}; $Ir_4(CO)_{11}$(t-BuNC), 2057 cm^{-1}; $Ir_4(CO)_{10}$(t-BuNC)$_2$, 2042 cm^{-1}; $Ir_4(CO)_9$(t-BuNC)$_3$, 2028 cm^{-1}. These stretching frequencies were shown to have a linear dependence upon concentration for $Ir_4(CO)_{12}$, $Ir_4(CO)_{11}(PPh_3)$, and $Ir_4(CO)_{11}$-

(t-BuNC). The reactions were run under pseudo-first order reaction conditions with the concentration of t-BuNC ranging from 10 to 400 times the concentrations of the cluster. The observed pseudo-first order rate constants were determined by monitoring the disappearance of the stretching frequencies of the starting material. Thus, a plot of ln (Abs_0/Abs) vs. time had a slope equal to k_{obs}. Plots such as these were reasonably linear for up to four half lives. At least four determinations of k_{obs} at each temperature were made with varying concentrations of t-BuNC. The second-order rate constant was then determined by plotting k_{obs} vs [t-BuNC] and measuring the slope. All slopes were measured using standard least-squares methods which also provided standard deviations of the slopes.

Results and discussion

Preparation

The use of $Me_3NO \cdot 2\,H_2O$ to facilitate carbonyl substitution in $Ir_4(CO)_{12}$ by phosphorus ligands and 1,5-cyclooctadiene leads to high yields of substituted products [5a,7]. Analogously, the reaction of $Ir_4(CO)_{12}$ in refluxing tetrahydrofuran with $Me_3NO \cdot 2\,H_2O$ and isonitriles (MeNC and t-BuNC) provides mixtures of the compounds $Ir_4(CO)_{12-x}(RNC)_x$ (x = 1—4; R = Me, t-Bu). These isonitrile derivatives are readily separated by TLC and isolated as air- and moisture-stable yellow solids. Refluxing tetrahydrofuran is necessary to dissolve $Ir_4(CO)_{12}$, but under these conditions direct substitution is significant and it is more difficult to control the product distribution for isonitrile- than for phosphorus-ligand substitution. In fact, the mono-isonitrile derivative $Ir_4(CO)_{11}$(RNC) (R = Me, t-Bu) is best prepared by the direct reaction of the ligand with a five-fold excess of $Ir_4(CO)_{12}$ in either refluxing tetrahydrofuran or refluxing chlorobenzene.

Solution structures

For all of the isonitrile compounds only infrared absorptions in the region (2140—2210 cm^{-1}) appropriate for terminal isonitrile ligands are observed. The methyl isonitrile derivatives $Ir_4(CO)_{12-x}(MeNC)_x$ (x = 1—4) display carbonyl stretching frequencies arising from terminal carbonyls only. Thus, these compounds appear to adopt structures related to the unbridged parent carbonyl cluster $Ir_4(CO)_{12}$ (2). Similarly, $Ir_4(CO)_{11}$(t-BuNC) and $Ir_4(CO)_{10}(t\text{-}BuNC)_2$ display bands attributable to terminal carbonyls only. However, both $Ir_4(CO)_9$(t-BuNC)$_3$ and $Ir_4(CO)_8(t\text{-}BuNC)_4$ have absorptions arising from bridging as well as from terminal carbonyl ligands.

The ^{13}C NMR spectra of $Ir_4(CO)_{12-x}(t\text{-}BuNC)_x$ (x = 1—4) display in each case only a single carbonyl resonance at room temperature. The limiting low temperature ^{13}C NMR spectrum of $Ir_4(CO)_{11}$(t-BuNC) (Fig. 1) shows five resonances of relative intensity two and one resonance of unit relative intensity all of which appear in the terminal carbonyl region (159.9 (2 C), 157.6 (2 C), 156.8 (2 C), 158.2 (2 C), 155.8 (2 C), and 155.0 (1 C) ppm). The signals of relative intensity two at 159.9, 157.6, 156.2, and 155.8 ppm have superimposed doublets arising from ^{13}C—^{13}C coupling (J = 11.5 Hz). These can be assigned to the four pairs of carbonyls which are *trans* to each other through

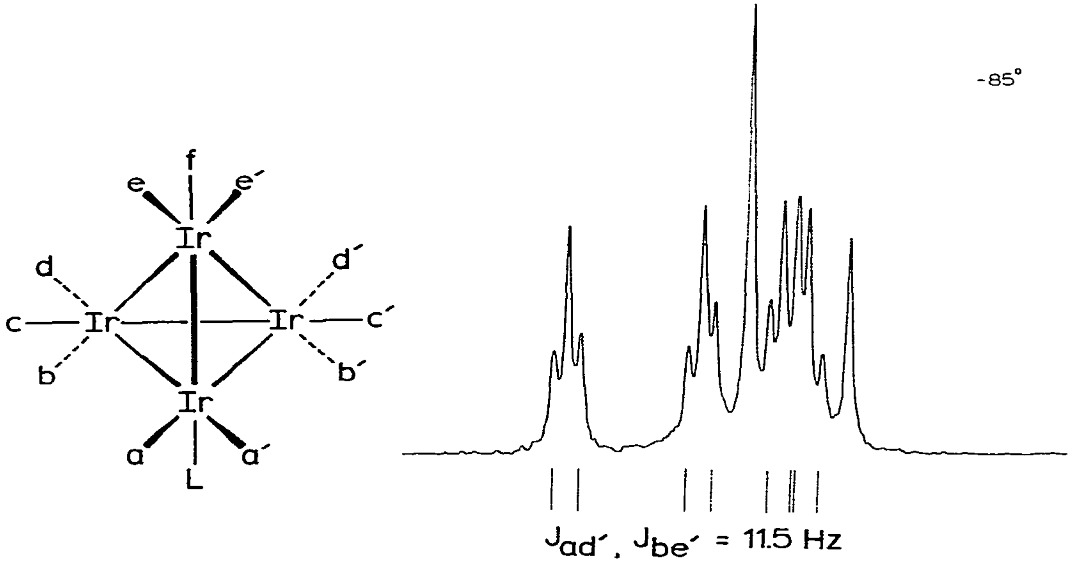


Fig. 1. Limiting low-temperature carbonyl ^{13}C NMR spectrum obtained for $Ir_4(CO)_{11}$(t-BuNC) (ca. 50% ^{13}CO-enriched).

Ir—Ir bonds (a, a'; d, d') and (b, b'; e, e') as indicated in Fig. 1. The remaining sharp signal of relative intensity two at 156.8 ppm can be assigned to carbonyls c and c'. These carbonyls are *trans* to each other, but they are magnetically equivalent and no coupling is observed. The signal of relative intensity one at 155.0 ppm is assigned to the unique carbonyl f. Since this carbonyl is *trans* to the non-^{13}C-enriched isonitrile ligand, no coupling is observed. This non-bridged structure of type 2 has been confirmed by X-ray crystallography [15].

The limiting low temperature ^{13}C NMR spectra of $Ir_4(CO)_{10}(t\text{-BuNC})_2$ and $Ir_4(CO)_9(t\text{-BuNC})_3$ (—90°C) display only resonances in the terminal carbonyl region (150—175 ppm). Both spectra are exceedingly complex, indicating the presence of several isomers. Four unbridged isomers (avoiding disubstitution on one iridium atom) are possible for $Ir_4(CO)_{10}(t\text{-BuNC})_2$. Similarly, nine isomers are possible for $Ir_4(CO)_9(t\text{-BuNC})_3$. Apparently, the energy differences between some of these isomers are relatively small and a complicated mixture results. The infrared spectrum of $Ir_4(CO)_9(t\text{-BuNC})_3$ indicates that at room temperature at least one isomer with bridging carbonyls also is present.

The limiting low temperature ^{13}C NMR spectrum (—94°C) of $Ir_4(CO)_8(t\text{-BuNC})_4$ displays resonances at 213.7, 178.3, 176.8, 164.5, 163.9 and 158.1 ppm. The signals in the terminal carbonyl region are of widely varying relative intensities indicating the presence of more than one isomer. However, the total relative intensity of these signals is five and the relative intensity of the bridging carbonyl resonance (214 ppm) is three. Thus, these isomers adopt carbonyl-bridged structures of type 1, presumably related to the structures of the phosphorus ligand derivatives [5,19].

The formation of bridging carbonyls in these derivatives appears to be largely the result of steric interactions. For relatively small ligands such as methyl isonitrile, repulsive interactions between the isonitrile and carbonyl ligands are slight and an unbridged structure results. With the more bulky t-butyl isonitrile ligands, steric interactions become larger and, for the tri- and tetra-substituted derivatives, carbonyl-bridged structures result. Similarly, for a very small phosphorus ligand such as $P(OMe)_3$, $Ir_4(CO)_{11}L$ exists as a mixture of carbonyl-bridged and unbridged isomers [19]. With higher levels of substitution or with larger phosphorus ligands, carbonyl-bridged isomers are observed exclusively. The presence of both bridged and unbridged isomers for $Ir_4(CO)_{11}(P(OMe)_3)$ and $Ir_4(CO)_9$(t-BuNC)$_3$ in solution is similar to the behavior observed for certain $YCCo_3(CO)_8L$ derivatives [20]. In contrast, the ^{13}C NMR spectrum of $Co_4(CO)_{11}(P(OMe)_3)$ shows the presence of only a bridged isomer [1b].

Stereodynamics of $Ir_4(CO)_{11}$(t-BuNC)

^{13}C NMR spectra for $Ir_4(CO)_{11}$(t-BuNC) at several temperatures are shown in Fig. 2. As the temperature is raised from —84° C to —40° C, the five two-carbon signals broaden, whereas the signal due to the single carbonyl f remains sharp. Notably, the spectrum at —56° C shows that the resonance due to c and c′ broadens more rapidly than the other two-carbon resonances. In the spectrum of —24° C the five two-carbon signals are coalesced into one hump and carbonyl f signal is beginning to broaden. By 40° C complete averaging of all carbonyls occurs.

The initial averaging process can be explained by the inverse of the process proposed by Cotton for $Rh_4(CO)_{12}$ [11] and demonstrated for $Ir_4(CO)_{11}(PPh_2Me)$ [5a]. Formation of carbonyl-bridged intermediates (see Fig. 3) with axial (3) or radial (4) isonitrile ligands leads to averaging of a, a′, b, b′, c, c′, d, d′, e, and e′. However, since *trans* relationships are maintained throughout the process, carbonyl f does not enter into the averaging process in accord with the spectrum at —40° C. The rapid broadening of carbonyls c and c′ is also consistent with this averaging process. An examination of the predicted site exchanges for the two combined intermediates 3 and 4 shows that carbonyls a, a′, b, b′, d, d′, e and e′ move into non-equivalent sites 50% of the time. In contrast, carbonyls c and c′ always move into non-equivalent sites and therefore should broaden more rapidly than the other signals. Radial and axial isomers are nearly equally populated in $Ir_4(CO)_{11}(PMe_3)$ [19], and since t-BuNC is less bulky than PMe_3, intermediates 3 and 4 should be essentially equal in energy and formed at identical rates.

A similar exchange involving an intermediate with two bridging carbonyls and one bridging isonitrile would also lead to scrambling of all carbonyls except f (see Fig. 4). However, a close examination of this site exchange process (Fig. 4) indicates that a, a′, c, c′, d, and d′ always move into non-equivalent sites, whereas b, b′, e, and e′ move into an equivalent site half of the time. Thus, the signals due to b, b′, e, and e′ would be expected to broaden less rapidly than the other signals. This is not compatible with the spectra observed for $Ir_4(CO)_{11}$(t-BuNC) between —84 and —40° C, and this process cannot be occurring to any appreciable extent over this temperature range.

At higher temperatures, complete scrambling of all eleven carbonyls occurs rapidly in $Ir_4(CO)_{11}$(t-BuNC), indicating the operation of an additional mechanism. No mechanistic information could be derived from the variable tempera-

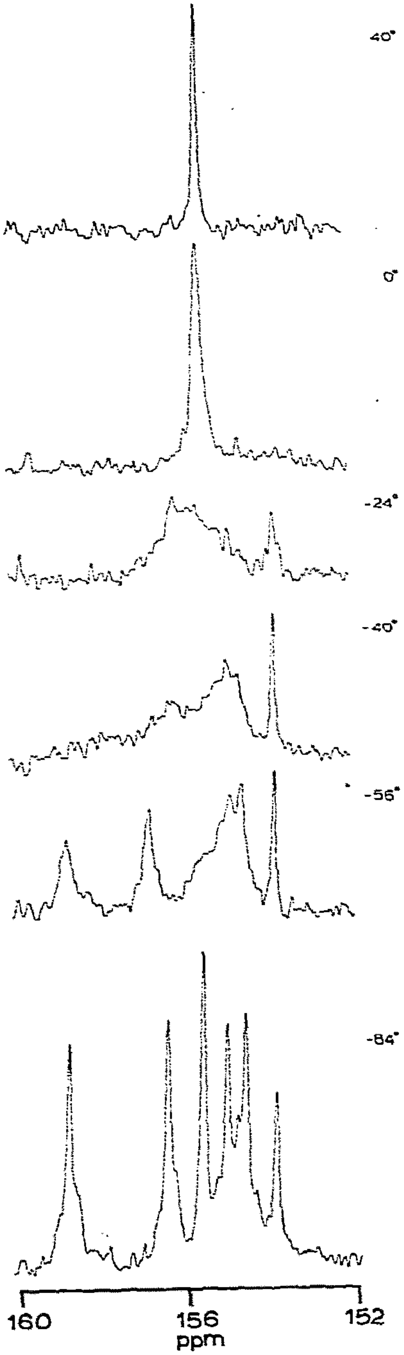


Fig. 2. Carbonyl ^{13}C NMR spectra obtained for $Ir_4(CO)_{11}$(t-BuNC) at various temperatures. Note that the ^{13}CO enrichment level is lower than for Fig. 1.

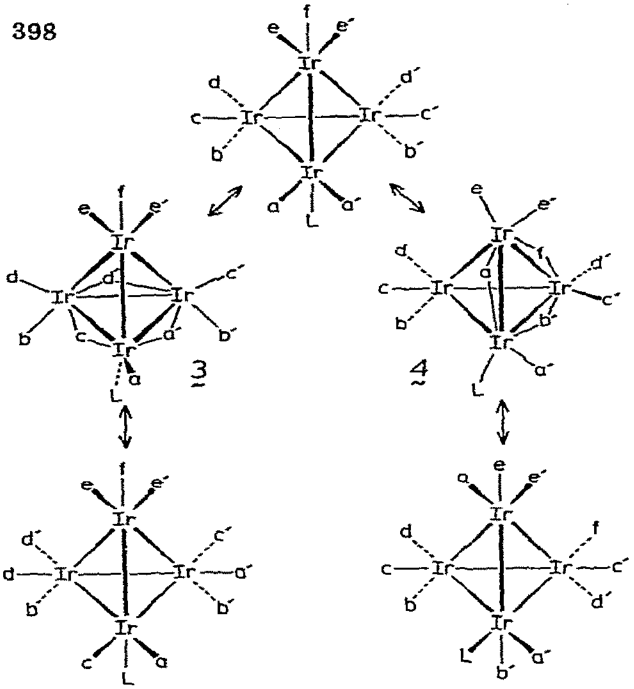


Fig. 3. Proposed mechanism of carbonyl site exchange in $Ir_4(CO)_{11}(t\text{-}BuNC)$.

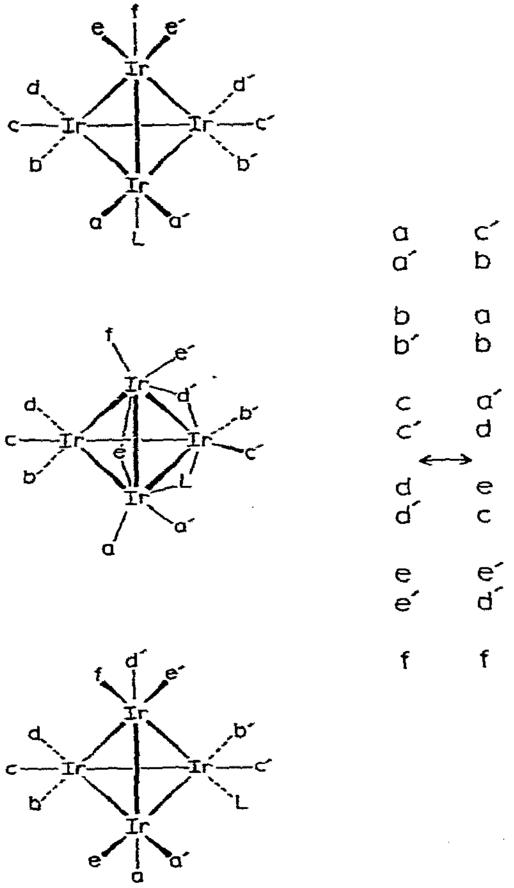


Fig. 4. Rearrangement process involving a bridging t-BuNC ligand with predicted carbonyl site exchanges.

ture ^{13}C NMR spectra of $Ir_4(CO)_{12-x}(t\text{-}BuNC)_x$ (x = 2—4), each set of which displays uniform line broadening and coalescence to a single signal.

Kinetics of substitution of $Ir_4(CO)_{12}$ by t-BuNC

Kinetic data have been obtained for each of the following stages of substitution of $Ir_4(CO)_{12}$ by t-BuNC.

$$Ir_4(CO)_{12} + t\text{-}BuNC \xrightarrow{k_1} Ir_4(CO)_{11}(t\text{-}BuNC)$$

$$Ir_4(CO)_{11}(t\text{-}BuNC) + t\text{-}BuNC \xrightarrow{k_2} Ir_4(CO)_{10}(t\text{-}BuNC)_2$$

$$Ir_4(CO)_{10}(t\text{-}BuNC)_2 + t\text{-}BuNC \xrightarrow{k_3} Ir_4(CO)_9(t\text{-}BuNC)_3$$

$$Ir_4(CO)_9(t\text{-}(BuNC)_3 + t\text{-}BuNC \xrightarrow{k_4} Ir_4(CO)_8(t\text{-}BuNC)_4$$

Pseudo-first order rate constants for the formation of $Ir_4(CO)_{11}(t\text{-}BuNC)$ at various temperatures and concentrations of t-BuNC are presented in Table 1. As an example Fig. 5 shows plots of the data obtained at 47.6°C. The slopes of these lines (k_{obs}) are shown plotted against the concentration of t-BuNC in Fig. 6. It is clear that k_{obs} shows a linear dependence on the concentration of t-BuNC and that within experimental error the intercept is not significantly different from zero. Thus, the substitution process of $Ir_4(CO)_{12}$ by t-BuNC is predominantly second order overall, depending on the concentration of both $Ir_4(CO)_{12}$ and t-BuNC. The second order rate constants (k_1) for this substitution at several temperatures are shown in Table 2. The slope of plot of $\ln(k_1/T)$ vs. $(1/T)$ (Fig. 7) was determined to be —6800 ± 250. The y-intercept was 13.8 ± 0.7. These data and the Eyring equation ($\ln(k/T) = \ln(k_B/h) + \Delta S^{\ddagger}/R$ —

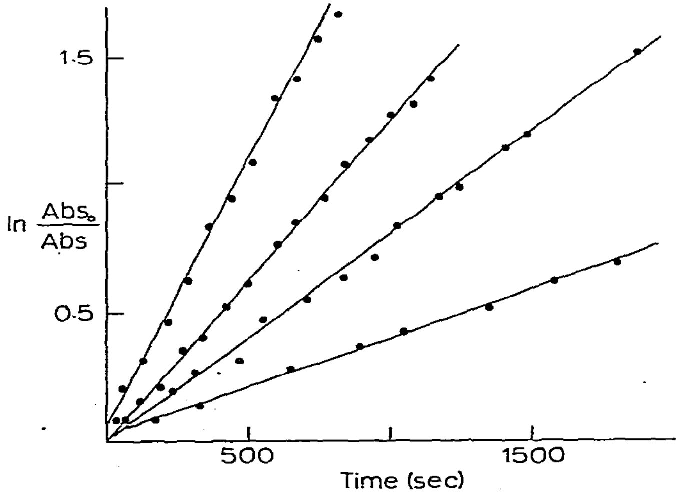


Fig. 5. Plot of $\ln(Abs_0/Abs)$ vs. time for the substitution of $Ir_4(CO)_{12}$ by t-BuNC at 47.6°C.

TABLE 1

PSEUDO-FIRST ORDER RATE CONSTANTS FOR THE SUBSTITUTION OF t-BuNC into $Ir_4(CO)_{12}$ AND ITS t-BuNC DERIVATIVES

Compound [a]	T (°C)	10^5 [t-BuNC] (M)	10^5 k_{obs} (sec^{-1}) [b]
$Ir_4(CO)_{12}$	69.0	129	69(3)
	69.0	161	103(2)
	69.0	194	127(2)
	69.0	242	172(3)
	69.0	387	274(4)
	59.0	484	177(2)
	59.0	581	201(2)
	59.0	678	248(3)
	59.0	775	285(3)
	47.6	194	38(1)
	47.6	387	80(1)
	47.6	775	123(2)
	47.6	1160	204(5)
	38.5	387	35(1)
	38.5	775	73(1)
	38.5	1160	112(1)
	38.5	1550	150(3)
	30.0	323	17(1)
	30.0	645	29(1)
	30.0	1290	65(2)
	30.0	1940	96(3)
$Ir_4(CO)_{11}$(t-BuNC)	28.3	484	96(2)
	28.3	807	136(3)
	28.3	1290	226(5)
	28.3	1940	308(9)
$Ir_4(CO)_{10}(t\text{-}BuNC)_2$	28.3	290	48(1)
	28.3	484	77(2)
	28.3	871	139(4)
	28.3	1610	247(10)
$Ir_4(CO)_9(t\text{-}BuNC)_3$	28.3	1610	47(1)
	28.3	3230	84(3)
	28.3	4840	123(4)

[a] T = 69.0°C and 59.0°C, $[Ir_4(CO)_{12}] = 17.1 \times 10^{-5}$ M; T = 47.6°C and 38.5°C, $[Ir_4(CO)_{12}] = 11.9 \times 10^{-5}$ M; T = 30.0°C, $[Ir_4(CO)_{12}] = 4.9 \times 10^{-5}$ M, $[Ir_4(CO)_{11}(t\text{-}BuNC)] = 13.4 \times 10^{-5}$ M, $[Ir_4(CO)_{10}(t\text{-}BuNC)_2] = 37.4 \times 10^{-5}$ M, $[Ir_4(CO)_9(t\text{-}BuNC)_3] = 76.6 \times 10^{-5}$ M. [b] Standard deviation given in parentheses.

$\Delta H^{\ddagger}/RT$) lead to values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 13.6 ± 0.5 kcal/mol and —20 ± 2 eu, respectively.

In a similar manner of the rate constants were determined for further substitution of $Ir_4(CO)_{11}$(t-BuNC) by t-BuNC, ultimately to give $Ir_4(CO)_8(t\text{-}BuNC)_4$. Table 1 displays the pseudo-first order rate constants determined at 28.3°C. In each case the reaction is linearly dependent on the concentrations of both the reacting cluster and t-BuNC. Plots of k_{obs} vs [t-BuNC] gave values of k_2, k_3, and k_4 at 28.3°C of 0.150(9), 0.153(2), and 0.025(1) M^{-1} sec^{-1} respectively. Finally, the substitution of $Ir_4(CO)_{11}(PPh_3)$ by t-BuNC at 28.3°C was also investigated and the pseudo-first order rate constants were found again to be linearly dependent on the concentration of t-BuNC, leading to a second order rate constant of 0.82(2) M^{-1} sec^{-1}.

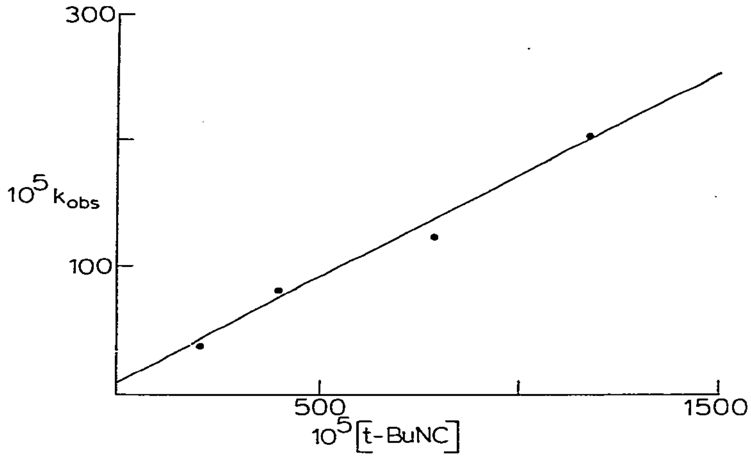


Fig. 6. Plot of pseudo-first order k_{obs} vs. [t-BuNC] for the substitution of $Ir_4(CO)_{12}$ by t-BuNC at 47.6°C.

The rate constants for the substitution of $Ir_4(CO)_{12}$ and $Ir_4(CO)_{11}(PPh_3)$ by t-BuNC at 28.3°C are summarized in Table 3. Also included are values for the successive substitution of $Ir_4(CO)_{12}$ by PPh_3 calculated for the same temperature from the data of Karel and Norton [13]. A direct comparison can be drawn between the first stage of substitution of $Ir_4(CO)_{12}$ by t-BuNC and by PPh_3, since a second order rate law is followed in both cases. Both reactions show a comparably negative value for $\Delta S^{\ddagger}$ (−20(2) vs. (−22(2) [13] eu), which is consistent with an associative mechanism. However, $\Delta H^{\ddagger}$ is significantly smaller for the case of t-BuNC (13.6(5) vs. 20.6(6) kcal/mole [13]), which causes the substitution of $Ir_4(CO)_{12}$ by t-BuNC to occur ca. 500,000 times more rapidly at 28.3°C than the analogous substitution by PPh_3.

This enormous difference in rate must be attributed to steric effects rather than to any electronic differences in the two ligands. The net donor/acceptor properties of a ligand (L) are reflected by the A_1 stretching frequency of $Ni(CO)_3L$ [21], which is 2064.1, 2068.9, 2071.3, and 2079.5 cm^{-1} for L = PMe_3, PPh_3, t-BuNC, and $P(OMe)_3$, respectively. These data indicate that t-BuNC is rather similar to PPh_3 in its bonding properties. On the other hand the cone angles [21] for the two ligands are markedly different, ca. 120° for t-BuNC and 145° for PPh_3, which allows for significantly easier penetration to

TABLE 2

SECOND ORDER RATE CONSTANTS FOR THE FORMATION OF $Ir_4(CO)_{11}$(t-BuNC)

T (°C)	k_1 (M^{-1} sec^{-1})
30.0	0.050(2)
38.5	0.099(1)
47.6	0.164(15)
59.0	0.383(9)
69.0	0.783(30)

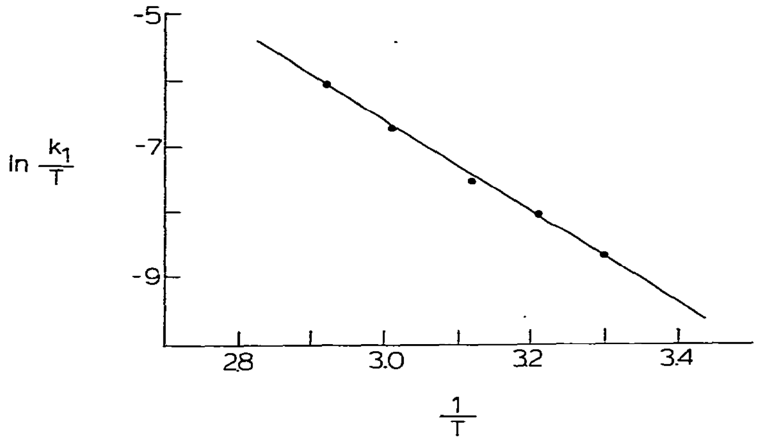


Fig. 7. Plot of lb(k_1/T) vs. $1/T$ for the substitution of $Ir_4(CO)_{12}$ by t-BuNC.

the metal center for the smaller isonitrile. Similarly, an associative pathway should predominate for other relatively small but reasonably nucleophilic ligands [8b,22].

The second order rate constants in Table 3 show some intriguing variations. The substitution of one carbonyl in $Ir_4(CO)_{12}$ appears to enhance the substitution of a second. The magnitude of this effect depends on the nature of the first ligand substituted, being ca. 3 for t-BuNC but ca. 16 for PPh_3. This difference most likely is due to the structural difference between $Ir_4(CO)_{11}$(t-BuNC) (configuration 2) and $Ir_4(CO)_{11}(PPh_3)$ (configuration 1), but this point deserves further study. Enhancement of further substitution is not observed. The rate of formation of $Ir_4(CO)_9$(t-BuNC)$_3$ is the same as that of $Ir_4(CO)_{10}$(t-BuNC)$_2$ but the rate of formation of $Ir_4(CO)_8$(t-BuNC)$_4$ drops significantly [23]. We attribute this fall-off in successive substitution rates to the increasing steric inhibition presented to the incoming ligand by first two and then three t-BuNC ligands already bound to the cluster framework.

TABLE 3

RATE CONSTANTS FOR THE SUBSTITUTION OF TETRAIRIDIUM CLUSTERS BY PPh_3 AND t-BuNC AT 28.3°C

Reactants	1st order rate constant (sec^{-1})	2nd order rate constant (M^{-1} sec^{-1})
$Ir_4(CO)_{12}$ + PPh_3		9×10^{-8} [a]
$Ir_4(CO)_{12}$ + t-BuNC		4.7×10^{-2}
$Ir_4(CO)_{11}(PPh_3)$ + PPh_3	5×10^{-8} [a]	
$Ir_4(CO)_{11}(PPh_3)$ + t-BuNC		8.2×10^{-1}
$Ir_4(CO)_{11}$(t-BuNC) + t-BuNC		1.5×10^{-1}
$Ir_4(CO)_{10}(PPh_3)_2$ + PPh_3	9×10^{-7} [a]	
$Ir_4(CO)_{10}$(t-BuNC)$_2$ + t-BuNC		1.5×10^{-1}
$Ir_4(CO)_9$(t-BuNC)$_3$ + t-BuNC		2.5×10^{-2}

[a] Calculated from $\Delta H^{\neq}$ and $\Delta S^{\neq}$ reported by Karel and Norton [13], error limits are less than one order of magnitude in each case.

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23 The rate constants have not been corrected statistically for the number of substitution sites (see ref. 13), since the precise structures of the derivatives $Ir_4(CO)_{12-x}(t\text{-}BuNC)_x$, $x = 2$—4, are not known.