Synthesis, Isolation, and Characterization of Trisodium Tricarbonyliridate (3−), Na₃[Ir(CO)₃]. Initial Studies on Its Derivative Chemistry and Structural Characterizations of *trans*-[Ir(CO)₃(EPh₃)₂]⁻, E = Ge, Sn, and *trans*-[Co(CO)₃(SnPh₃)₂]⁻ [†,1]

**Jessica M. Allen, William W. Brennessel, Carrie E. Buss, John E. Ellis,*,‡
Mikhail E. Minyaev, Maren Pink, Garry F. Warnock, Mark L. Winzenburg, and
Victor G. Young, Jr.**

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Reduction of Na[Ir(CO)₄] by sodium metal in (Me₂N)₃PO, followed by treatment with liquid ammonia, provided high yields (ca. 90%) of unsolvated Na₃[Ir(CO)₃], a thermally stable, pyrophoric orange solid. This substance contains iridium in its lowest known formal oxidation state of −3 and has been characterized by IR spectroscopy, elemental analyses, and derivative chemistry, i.e., by its conversion to the triphenylgermyl and triphenylstannyl complexes, *trans*-[Ir(CO)₃(EPh₃)₂]⁻, E = Ge, Sn. Single-crystal X-ray structures of the tetraethylammonium salts of these species, as well as [Co(CO)₃(SnPh₃)₂]⁻, confirm the trigonal bipyramidal nature of the anions, originally predicted on the basis of their IR spectra in the carbonyl stretching frequency region. These structural characterizations provide important additional evidence for the presence of metal tricarbonyl units in Na₃[M(CO)₃], M = Co, Ir.

Introduction

Metal carbonyl anions are important precursors to a tremendous variety of organometallic, inorganic, and organic species.[2] They are also of interest as the first compounds to contain transition metals in negative formal oxidation states,[3] i.e., [Co(CO)₄]⁻ and [Fe(CO)₄]²⁻, which were originally reported more than 60 years ago.[4] These anions have been shown to mimic halides, e.g., I⁻, and chalcogenides, e.g., S²⁻, respectively, in many of their chemical reactivity patterns.[5] The existence of main group atomic trianion salts, e.g., Na₃P, suggested that electronically equivalent or isolobal metal carbonyl trianions should also be capable of existence.[6] About 25 years ago the first compounds of this class, i.e., Na₃[M(CO)₄] = Mn, Re, were obtained via reductions of the respective pentacarbonylmetalates(1−) of these elements.[7] Soon afterward, tricarbonylcobaltate(3−), along with several others containing 3d, 4d, and 5d elements, were reported.[8] These species are of

substantial interest since they contain transition metals in their lowest known formal oxidation states,[3] and for this reason they have been referred to as "super-reduced" metal carbonyls.[9] In the original report on [Co(CO)₃]³⁻, a formally analogous iridium complex was also described,[10] but no full account of the iridium research has been available to date. The claimed existence of [Ir(CO)₃]³⁻ was based mainly on IR spectral and derivative studies, e.g., its reactions with Ph₃ECl, E = Ge, Sn, to provide the respective [Ir(CO)₃(EPh₃)₂]⁻.[10] Recently, tetraethylammonium salts of the latter, along with the related [Co(CO)₃(SnPh₃)₂]⁻, were characterized by single-crystal X-ray structural studies. By this method, the presence of tricarbonylmetal units in these derivatives and, by inference, in the analogous carbonylmetalate-(3−) precursors was established for the first time. In this article we describe these structural studies along with the first full account of the synthesis, isolation, and characterization of Na₃-[Ir(CO)₃], the only known Ir(III−) species.

Experimental Section

General Procedures and Starting Materials. All operations were performed under an atmosphere of 99.9% argon or 99.5% carbon monoxide, further purified by passage through columns of activated BASF catalyst and molecular sieves. Also, the CO was passed through a column of Ascarite, which is a trade name for a self-indicating sodium hydroxide nonfibrous silicate formulation, for the quantitative absorption of CO₂. Similar products used by microanalysts should provide satisfactory results. All connections involving the gas purification systems were made of glass, metal, or other materials impermeable to air.[11] Solutions were transferred via stainless steel double-ended needles (cannulas) whenever possible. Standard Schlenk techniques were

† Dedicated to Professor Alan Davison, F.R.S., of MIT on the occasion of his 65th birthday.

‡ E-mail: ellis@chem.umn.edu.

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employed with a double-manifold vacuum line.[11-14] Unless otherwise stated below, all starting materials were obtained from commercial sources and freed from oxygen and moisture before use and all reaction mixtures were stirred with glass-covered magnetic stir bars. The preparation of $[Et_4N][Co(CO)_3(SnPh_3)_2]$ was carried out as previously described.[10] Solvents were freed of impurities by standard procedures.[11] Liquid ammonia was distilled from sodium metal. Hexamethylphosphoramide (HMPA) was twice distilled in vacuo, first from calcium hydride and then from a small piece of sodium, which first dissolved at room temperature to provide a homogeneous deep blue solution. (**CAUTION:** *HMPA should be handled with extreme care as it is a potential carcinogen!*) HMPA solutions of $Na_3[Ir(CO)_3]$ for infrared spectra were very difficult to obtain free of oxidation products and were prepared in a Vacuum Atmosphere Corporation drybox and transferred into sealed CaF_2 solution cells that had been previously purged with dilute blue solutions of Na in HMPA to remove absorbed moisture, oxygen, and other potential oxidants. Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer or a Mattson 6021 FTIR spectrometer with samples in 0.1 mm sealed NaCl or CaF_2 cells. Nujol (mineral oil) mulls of air-sensitive solids were prepared in an argon-filled drybox. NMR samples were sealed in 5 mm tubes and were run on Varian Unity-300, Nicolet NT-300 WB, or IBM NR-300 AF spectrometers. Melting points are uncorrected and were obtained in sealed capillaries on a Thomas-Hoover unimetal apparatus. Microanalyses were carried out by H. Melissa and G. Reuter Analytical Laboratories, Engelskirchen, Germany.

Na[Ir(CO)₄] (1). The method of Malatesta et al. was employed.[15] Typically, $Ir_4(CO)_{12}$ (0.98 g, 0.89 mmol) was added to excess sodium sand[16] (1.20 g, 52 mmol) in a round-bottom flask. Tetrahydrofuran (20 mL) was transferred via cannula to the flask containing the reactants, and the inert atmosphere was replaced with carbon monoxide at ambient pressure. The reaction mixture slowly acquired a red hue as it was stirred. After 24 h, a clear pale yellow solution of $Na[Ir(CO)_4]$ was separated from muddy brown suspended solids via filtration. Removal of solvent in vacuo provided 0.69 g (60% yield, if unsolvated, based on $Ir_4(CO)_{12}$) of colorless powdery **1**, which appeared to be essentially free of THF, based on its fluorolube mull IR spectrum. IR (mineral oil mull) $\nu(CO)$: 2018 w, 1938 sh, 1871 vs (br) cm^{-1}. IR (THF solution) $\nu(CO)$: 1892 vs, 1856 sh cm^{-1}. The latter spectrum is in substantial agreement with that originally reported by Malatesta and co-workers.[15] The solid was of marginal thermal stability and darkened to a tan color after several days at room temperature. Due to its thermal instability, no satisfactory elemental analyses could be obtained, but it was converted to a thermally stable $[Ph_4As]^+$ salt, vide infra.

[Ph₄As][Ir(CO)₄] (2). Reduction of $Ir_4(CO)_{12}$ (0.400 g, 0.362 mmol) by excess 0.75% sodium amalgam (7.0 mL; 0.71 g, 31 mmol Na) in THF (40 mL) was carried out with vigorous stirring under an atmosphere of carbon monoxide. Three days were required before the reduction was mostly complete, but IR spectra still showed the presence of small amounts of less reduced carbonyl iridates. The resulting pale brown solution of $Na[Ir(CO)_4]$ was separated from the excess sodium amalgam via decantation and added to a solution of $[Ph_4As]Cl$ (0.66 g, 1.5 mmol) in 80 mL of water at 0 °C. The resulting brown solid was isolated on a coarse porosity fritted disk, carefully washed with 20 mL of water, and dried in vacuo. Crystallization from THF/ether, followed by washing with isopentane and drying in vacuo at room temperature, afforded 0.52 g (52% yield based on $Ir_4(CO)_{12}$) of homogeneous yellow crystalline **2** of satisfactory purity. Anal. Calcd for $C_{28}H_{20}AsIrO_4$ (%): C, 48.91; H, 2.93. Found (%): C, 48.81; H,

3.01. IR (mineral oil mull) $\nu(CO)$: 1908 sh, 1893 vs cm^{-1}. IR (THF solution) $\nu(CO)$: 1891 vs cm^{-1}. Crystalline **2** is stable in air for brief periods but should be stored under anaerobic conditions. Unlike **1**, solid **2** appears to be stable indefinitely at room temperature. Solutions of **2** in THF are very air sensitive.

Na₃[Ir(CO)₃] (3). Colorless **1** (0.66 g, 2.0 mmol, assuming **1** is unsolvated) was combined with sodium sand (0.15 g, 6.5 mmol) in a round-bottom flask. Freshly distilled HMPA (15 mL) was added, and the reaction mixture was stirred under dynamic vacuum (ca. 0.01 Torr) for 12 h at 20 °C. The resulting dark yellow solution was then frozen at −78 °C, and anhydrous ammonia (60 mL) was added via cannula. The mixture was stirred at reflux (ca. −33 °C) until the solvents had completely mixed. A yellow-orange precipitate in a deep yellow-red solution was present after 2 h. The reaction mixture was cooled to −78 °C and filtered at −78 °C using a previously described jacketed filtration unit.[17a] After the solid was washed thoroughly with liquid ammonia (4 × 50 mL), it was dried in vacuo at room temperature to provide 0.63 g (90% yield based on unsolvated **1**) of orange powder, which provided satisfactory analysis for unsolvated **3**. Anal. Calcd for $C_3IrNa_3O_3$ (%): C, 10.44; H, 0.00; Na, 19.98. Found (%): C, 10.17; H, 0.15; Na, 19.84. IR (mineral oil mull) $\nu(CO)$: 1805 w sh, 1642 vs (br) cm^{-1}. IR (HMPA) $\nu(CO)$: 1666 vs (br) cm^{-1}. No N−H or C−H absorptions were present in fluorolube mull spectra of **3**. Compound **3** was exceedingly air sensitive and observed to slowly darken without melting between 200 and 300 °C under an inert atmosphere.

[Et₄N][Ir(CO)₃(SnPh₃)₂] (4). Route a: From Ir₄(CO)₁₂. $Ir_4(CO)_{12}$ (0.57 g, 0.52 mmol) was reduced by excess sodium sand (0.170 g, 30 mmol) in 10 mL of THF under an atmosphere of carbon monoxide as described above in the synthesis of **1**. Following filtration to remove the excess sodium metal, all solvent was removed in vacuo. The resulting colorless dry salt was then treated with sodium sand (0.142 g, 6.2 mmol, 3.0 equiv based on $Ir_4(CO)_{12}$) and stirred in 70 mL of liquid ammonia for 3 h at −60 °C to give the usual yellow-orange reaction mixture. Subsequently, solid Ph_3SnCl (1.81 g, 4.70 mmol) was added rapidly, via a bent Schlenk tube, to the reaction mixture. A white suspension rapidly formed. After 1.5 h, solid $[Et_4N]Br$ (0.70 g. 3.3 mmol) was added and the reaction mixture was stirred for about 2 h at −78 °C. Following evaporation of the liquid ammonia, the resulting ivory solid was washed with diethyl ether (5 × 20 mL) to remove traces of ammonia, dissolved in 20 mL of THF, and filtered through a medium-porosity fritted disk. Addition of excess heptane to the filtrate gave pale yellow crystals. Recrystallization from THF/absolute ethanol afforded 1.06 g (46% based on $Ir_4(CO)_{12}$) of colorless needles of satisfactorily pure **4**, which began to decompose without melting at about 160 °C. Anal. Calcd for $C_{47}H_{50}IrNO_3Sn_2$ (%): C, 51.07; H, 4.55; N, 1.27. Found (%): C, 51.14; H, 4.65; N, 1.27. IR (mineral oil mull) $\nu(CO)$: 1980 w, 1911 sh, 1901 s cm^{-1}. IR (THF) $\nu(CO)$: 1924 vs, 1912 sh cm^{-1}. ^1H NMR (300 MHz, acetone-d_6, 25 °C): $\delta = 7.1 - 7.4$ (m, 30 H, SnPh$_3$), 3.1 (q, 8H, CH$_2$ of Et$_4$N), 1.2 (tt, 12 H, CH$_3$ of Et$_4$N), ppm. Compound **4** appears to be stable indefinitely in the solid state toward air oxidation at room temperature. It dissolves in CH_2Cl_2, THF, *N,N*-dimethylformamide, CH_3CN, acetone, and HMPA to provide only slightly air sensitive solutions. For example, a THF solution of **4** was allowed to evaporate slowly in air to give long colorless needles of pure **4**.

Route b: From Na[Ir(CO)₄] (1). Freshly prepared **1**, (0.25 g, 0.76 mmol) was reduced by a slight excess of sodium metal (0.0580 g, 2.52 mmol, 3.2 equiv) in 40 mL of liquid ammonia to rapidly produce a slurry of yellow-orange solid, which was shown in other studies to be an inseparable mixture of $Na_3[Ir(CO)_3]$ and $Na_2C_2O_2$. At −78 °C, a solution of Ph_3SnCl (0.95 g, 2.5 mmol, 3.2 equiv) in 10 mL of THF was added via cannula. The remainder of the procedure was identical to that of route a, except the product was recrystallized from acetone/ether to provide 0.74 g (87% based on $Na[Ir(CO)_4]$) of colorless microcrystals that were identical to bona fide **4**, obtained by route a.

[Et₄N][Ir(CO)₃(GePh₃)₂] (5). $Ir_4(CO)_{12}$ (0.50 g, 0.45 mmol) was reacted with sodium sand (0.18 g, 7.8 mmol) in HMPA (20 mL) for 2

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Table 1. Crystal Data, Data Collection, Solution, and Refinement for **4**, **5**, and **6** as CH_2Cl_2 Solvates

compd	**4**·CH_2Cl_2	**5**·CH_2Cl_2	**6**·CH_2Cl_2
empirical formula	$C_{48}H_{54}Cl_2IrNO_3Sn_2$	$C_{48}H_{52}Cl_2Ge_2IrNO_3$	$C_{48}H_{52}Cl_2CoNO_3Sn_2$
formula mass	1191.39	1099.19	1058.12
cryst habit, color	block, colorless	block, colorless	block, colorless
cryst size, mm	$0.12 \times 0.12 \times 0.12$	$0.17 \times 0.16 \times 0.05$	$0.10 \times 0.10 \times 0.08$
cryst syst	monoclinic	monoclinic	monoclinic
space group	Cc	Cc	Cc
a, Å	23.933(2)	23.722(3)	23.804(1)
b, Å	9.858(1)	9.780(1)	9.8380(5)
c, Å	20.785(2)	20.679(2)	20.788(1)
α, deg	90.00	90.00	90.00
β, deg	105.913(2)	106.946(2)	106.819(1)
γ, deg	90.00	90.00	90.00
v, Å	4715.9(8)	4589.2(9)	4660.0(4)
Z	4	4	4
ρ_{calcd}, g cm^{-3}	1.678	1.591	1.508
μ(Mo Kα), mm^{-1}	4.019	4.351	1.570
$F(000)$	2328	2184	2128
temp (K)	173(2)	173(2)	173(2)
θ range (deg)	1.77–27.51	1.79–27.52	1.79–27.48
completeness to $\theta = 27.51$ (%)	98.9	99.5	99.6
index range	$-31 = h = 27$	$-30 = h = 27$	$-30 = h = 30$
	$-12 = k = 12$	$-12 = k = 12$	$-12 = k = 12$
	$-26 = l = 26$	$-26 = l = 26$	$-26 = l = 26$
rflns collected	23708	20663	23428
unique rflns	9708	9783	10092
R(int)^a	0.0321	0.0408	0.0434
obsd data	9066	8993	8217
variables	518	518	518
absolute structure param	0.012(3)	0.004(5)	0.004(14)
weighting params $-a$, b^b	0.0249, 4.4766	0.0378, 0.0000	0.0179, 0.0000
GOF on $F^{2\ c}$	1.057	1.024	0.922
R1/wR2 indices with $I > 2\sigma(I)^{d,e}$	0.0278/0.0580	0.0351/0.0733	0.0330/0.0501
R1/wR2 indices (all data)	0.0320/0.0591	0.0413/0.0759	0.0501/0.0538
largest peaks and holes, e Å^{-3}	0.672/−0.537	1.548/−0.537	0.500/−0.401

^{a} $R_{int} = \Sigma|F_o^2 - \langle F_c^2 \rangle|/\Sigma|F_o^2|$. ^{b} Weighting scheme: $w = q/\sigma^2(F_o^2) + (aP)^2 + bP$ and $P = (F_o^2 - 2F_c^2)/3$. ^{c} GOF = $S = \Sigma[w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$. ^{d} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{e} wR2 = $[\Sigma[w(|F_o^2| - |F_c^2|)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

h in vacuo (ca. 0.01 Torr) at room temperature. The final reaction mixture was deep blue due to excess sodium. After 12 h at room temperature, it had changed to a deep red color. Solid Ph₃GeCl (1.00 g, 5.4 mmol) was added, and, after being stirred for 3 h at room temperature, the reaction mixture was a paler red hue. Transfer of this mixture to an excess of Et₄N⁺ Br⁻ (1.5 g, 7 mmol) in 100 mL of water gave a gummy orange precipitate. After decanting the excess liquid from the solid, the latter was dried in vacuo and dissolved in 15 mL of THF. Following filtration, all but about 5 mL of THF was removed to provide tan crystals in a deep red solution. Addition of excess absolute ethanol caused the remaining product to precipitate. The resulting product was washed with diethyl ether and dried in vacuo. Recrystallization from THF/ether gave 0.67 g (36%) of silvery pale green crystalline **5**, which provided satisfactory elemental analyses and decomposed without melting at about 145 °C. Anal. Calcd for C₄₇H₅₀-Ge₂IrNO₃ (%): C, 55.65; H, 4.97; N, 1.38. Found (%): C, 55.90; H. 5.14, N, 1.00. IR (mineral oil mull) v(CO): 1982 w, 1914 sh, 1899 s cm⁻¹; (THF) v(CO): 1930 vs, 1914 sh cm⁻¹. ¹H NMR: (300 MHz, acetone-d_6, 25 °C) δ = 7.0 − 7.7 (m, 30 H, GePh₃), 3.1 (q, 8 H, CH₂ of Et₄N), 1.2 (tt, 12 H, CH₃ of Et₄N) ppm. Compound **5**, like **4**, is also stable indefinitely in air at room temperature in microcrystalline form. It also has solubility properties similar to those of **4**; however, solutions of **5** in air deteriorate more rapidly than those of **4**. Pure **4** is colorless, but **4** is pale green when very slightly oxidized.
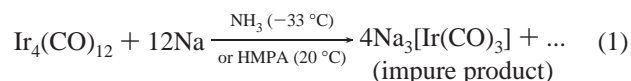
X-ray Structure Determinations of 4, 5, and [Et₄N][Co(CO)₃-(SnPh₃)₂] (6). Heptane was slowly layered on nearly saturated solutions of **4**, **5**, and **6** in CH_2Cl_2, at room temperature. After 1−2 days, X-ray quality colorless block-shaped crystals had formed. A crystal of each compound was placed on the tip of a 0.1 mm glass capillary and mounted on a Siemens SMART Platform CCD diffractometer for data collection (Mo Kα radiation with λ = 0.71073 Å was employed), which was carried out at −100 °C. A randomly oriented region of reciprocal space was surveyed to the extent of a full sphere (**4**) and 1.3 hemispheres (**5**, **6**) to a resolution of 0.77 Å ($2\theta_{max}$ = 55.0°). Major sections of

frames were collected with 0.30° steps in ω. For all structures, the program SADABS was used to correct the data for absorption.[17b] Final cell constants were calculated from 6621 (**4**), 4978 (**5**), and 8106 (**6**) strong reflections after integration by the program SAINT 6.01.[17c]

All structures were solved by the Patterson method, refined by full-matrix least squares minimization on F^2 and Fourier techniques using the SHELXTL-PLUS suite of programs (SHELXTL-Plus V 5.4, Bruker Analytical X-Ray Systems, Madison, WI). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. Crystal data, data collection, solution, and refinement information for **4**, **5**, and **6** are shown in Table 1. Additional crystallographic details are found in the Supporting Information.
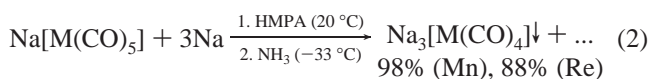
Results and Discussion

Syntheses and Isolation of Na₃[Ir(CO)₃]. Original syntheses of tricarbonyliridate(3−) involved the direct reduction of Ir₄-(CO)₁₂ by solutions of sodium metal in liquid ammonia or hexamethylphosphoramide (HMPA)[10] (eq 1). All attempts to
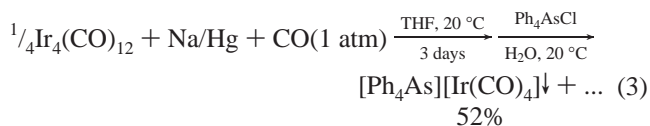
$$Ir_4(CO)_{12} + 12Na \xrightarrow[\text{or HMPA (20 °C)}]{NH_3\ (-33\ °C)} 4Na_3[Ir(CO)_3] + ... \quad (1)$$
$$\text{(impure product)}$$

isolate satisfactorily pure salts of $[Ir(CO)_3]^{3-}$ from these reactions were unsuccessful. Invariably, the latter were contaminated by polynuclear carbonyliridates, which Malatesta and co-workers showed, many years ago, to form via alkali metal reductions of Ir₄(CO)₁₂, even when conducted under an atmosphere of CO.[15,18a]

Subsequently, it was discovered that high yields of satisfactorily pure samples of unsolvated Na₃[M(CO)₄], M = Mn, Re,

were available by sodium metal reductions of the respective $Na[M(CO)_5]$ in HMPA, followed by addition of excess liquid ammonia[7b] (eq 2). For this reason, we investigated the analogous

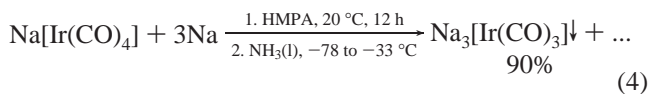$$Na[M(CO)_5] + 3Na \xrightarrow[\text{2. NH}_3 \, (-33\,°C)]{\text{1. HMPA (20 °C)}} Na_3[M(CO)_4]\!\downarrow + \ldots \quad (2)$$
$$98\% \text{ (Mn)}, 88\% \text{ (Re)}$$

reduction of $Na[Ir(CO)_4]$, a thermally unstable and very air sensitive colorless solid. Although $[Ir(CO)_4]^-$ was reported by Hieber in 1940,[18a] Malatesta and co-workers[15,18b] were the initial group to characterize this substance and describe solutions of $Na[Ir(CO)_4]$. However, to the best of our knowledge, the first details of its isolation are reported herein. Also, we describe its metathesis with $[Ph_4As]Cl$ to produce a new thermally stable and satisfactorily pure tetraphenylarsonium salt, $[Ph_4As][Ir(CO)_4]$ (eq 3). The yield of the tetracarbonyliridate(1−) salt is

$$^{1}/_{4}Ir_4(CO)_{12} + Na/Hg + CO(1 \text{ atm}) \xrightarrow[\text{3 days}]{\text{THF, 20 °C}} \xrightarrow[\text{H}_2\text{O, 20 °C}]{\text{Ph}_4\text{AsCl}}$$
$$[Ph_4As][Ir(CO)_4]\!\downarrow + \ldots \quad (3)$$
$$52\%$$

only moderate, ca. 52%, because the initial sodium amalgam or sodium sand reductions of $Ir_4(CO)_{12}$ provided only about 60% yields of $Na[Ir(CO)_4]$. IR spectra of both the isolated Na^+ and $[Ph_4As]^+$ salts of $[Ir(CO)_4]^-$ in the $\nu(CO)$ region are in good agreement with that of the bis(triphenylphosphine)iminium salt, $[PPN][Ir(CO)_4]$. Martinengo and co-workers previously obtained this thermally stable material in 75% isolated yield by a reductive carbonylation of $IrCl_3(H_2O)_3$.[18c]

Reduction of $Na[Ir(CO)_4]$ by sodium in HMPA at room temperature, under a dynamic (ca. 0.01 Torr) vacuum, provided after 12 h a dark yellow solution. Following precipitation with excess liquid ammonia at −78 °C, a homogeneous, pyrophoric orange powder was isolated. Satisfactorily pure and thermally robust $Na_3[Ir(CO)_3]$, dec ≥200 °C, was thereby obtained in 90% yield based on unsolvated $Na[Ir(CO)_4]$ (eq 4). Mineral oil mull IR spectra of $Na_3[Ir(CO)_3]$ indicated that the product was spectroscopically free of ammonia and HMPA, vide infra. Corresponding reductions of $Na[Rh(CO)_4]$ also gave $Na_3[Rh(CO)_3]$,[8,19] but $Na[Co(CO)_4]$ was found to be totally inert toward reduction in HMPA, under otherwise identical conditions.[20]

$$Na[Ir(CO)_4] + 3Na \xrightarrow[\text{2. NH}_3(l),\, -78 \text{ to } -33\,°C]{\text{1. HMPA, 20 °C, 12 h}} Na_3[Ir(CO)_3]\!\downarrow + \ldots$$
$$90\%$$
$$(4)$$

HMPA solution IR spectra of $Na_3[Ir(CO)_3]$ in the $\nu(CO)$ region consist of one intense, broad and symmetric absorption centered at 1665 (±5) cm^{-1}. The corresponding spectrum of $Na_3[Rh(CO)_3]$ in HMPA[8] is virtually identical, indicating that the iridate(3−) and rhodate(3−) are likely to have very similar structures in solution. Mineral oil mull IR spectra of $Na_3[Ir(CO)_3]$ in the $\nu(CO)$ region are nearly identical to those in HMPA solution, which suggests that the environments of $[Ir(CO)_3]^{3-}$ in solution and in the solid state are similar. These spectra are consistent with the presence of trigonal planar $[Ir(CO)_3]^{3-}$ units, for which only one IR active carbonyl stretching frequency is expected. However a crystal structure

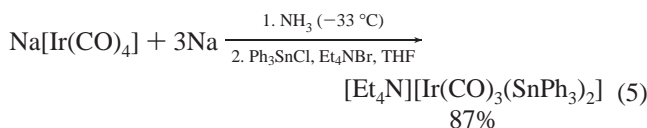determination will be essential to unambiguously establish the nature of this unique iridium complex.

^{1}H NMR spectra of approximately 0.1 M HMPA-d_{18} solutions of freshly prepared $Na_3[Ir(CO)_3]$ at room temperature almost invariably showed a *very weak* singlet at δ −15.2 ppm, suggesting that most of the iridium species in solution was nonhydridic in nature. Addition of 1 equiv of ethanol caused the resonance at −15.2 ppm to dramatically increase in intensity. Introduction of a second equivalent of ethanol caused the signal at −15.2 ppm to disappear, and a new intense singlet at −12.3 was observed. Attempts to isolate the latter species as a pure substance have not been successful to date. Infrared mineral oil mull spectra in the $\nu(CO)$ region of an impure and thermally unstable Ph_4As^+ salt showed an intense band at 1880 cm^{-1}, which is *not* coincident with that of bona fide $[Ph_4As][Ir(CO)_4]$, vide supra. Since the IR spectrum of the impure product in the $\nu(CO)$ region exhibits a band pattern and intensity very similar to those of *trans*-$[Ir(CO)_3(EPh_3)_2]^-$, E = Ge, Sn, vide infra, this salt is postulated to contain *trans*-$[Ir(CO)_3H_2]^-$ units. However, it will be necessary to unambiguously determine the composition of this species by ^{1}H and ^{13}C NMR spectra of the 99%-enriched [13]CO-labeled complex before a definitive formulation is possible.

Germylation and Stannylation of $Na_3[Ir(CO)_3]$: Synthesis and Isolation of $[Ir(CO)_3(EPh_3)_2]^-$, E = Ge, Sn. More than 40 years ago Hein established that carbonylmetalates react with Ph_3EX, E = Ge, Sn, X = Cl, Br, OH, to provide bi- or polymetallic derivatives that are generally much less reactive and consequently easier to handle and purify than the parent metal carbonyl salts.[21] This important derivatization method is now recognized to be one of the best strategies in obtaining initial evidence for the existence of highly reactive and/or thermally unstable mononuclear homoleptic carbonyl,[3] isocyanide,[22] alkyne,[23] or organophosphane[24] metalates, as well as related mixed-ligand versions thereof.[25]

As mentioned above, direct reduction of $Ir_4(CO)_{12}$ by 12 equiv of sodium metal in liquid ammonia or HMPA invariably resulted in unsatisfactory conversion to $Na_3[Ir(CO)_3]$. Reactions of these solutions with 2 equiv of Ph_3GeCl or Ph_3SnCl, followed by cation exchange with tetraethylammonium bromide and workup, provided only 35−45% yields of colorless microcrystals of satisfactorily pure $[Et_4N][Ir(CO)_3(EPh_3)_2]$, E = Sn **4** or Ge **5**, respectively. Compound **5** was only prepared by this procedure in HMPA. In contrast, when $Na[Ir(CO)_4]$ was reduced by sodium metal in liquid ammonia, followed by addition of 3 equiv of Ph_3SnCl and metathesis with Et_4NBr, the isolated yield of **4** increased to 87% (eq 5). The latter procedure, or an analogous one employing HMPA for reactants/products unstable in liquid

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$$Na[Ir(CO)_4] + 3Na \xrightarrow[\text{2. Ph}_3\text{SnCl, Et}_4\text{NBr, THF}]{\text{1. NH}_3\ (-33\ °\text{C})}$$

$$[Et_4N][Ir(CO)_3(SnPh_3)_2] \quad (5)$$
$$87\%$$

ammonia, would appear to be the method of choice for future studies of the chemical properties of Na₃[Ir(CO)₃], which remain very poorly explored. Compounds **4** and **5** are air stable indefinitely at room temperature as microcrystalline solids. They readily dissolve in polar solvents such as tetrahydrofuran, dichloromethane, and acetonitrile to provide colorless solutions, which only slowly deteriorate in air under ambient conditions.

Solution IR spectra of **4** and **5** in THF in the ν(CO) region exhibit only one strong symmetrical absorption at 1924 and 1930 cm⁻¹, respectively. Closely related neutral and cationic iridium tricarbonyl complexes Ir(CO)₃(PPh₃)(SnPh₃)[26] and [Ir(CO)₃-(PMe₂Ph)₂]⁺ [27] also showed intense single absorptions at 1965 and 2000 cm⁻¹, respectively, which indicated the presence of trigonal bipyramidal species with carbonyls in trigonal positions, in accord with Rossi and Hoffman's conclusions.[28] Structural characterizations of [Ir(CO)₃(PMe₂Ph)₂]⁺ [29] and [Ir(CO)₃(PCy₃)-(SnPh₃)[30] confirmed the presence of *trans*-Ir(CO)₃L₂ units for these formally d⁸ Ir(I) complexes. These results, along with the ¹H NMR spectral data, provide strong evidence that solutions of **4** and **5** contain *trans*-[Ir(CO)₃(EPh₃)₂]⁻ molecules, which represent the first known five-coordinate carbonyliridates. On the basis of the IR ν(CO) spectral data, **4** and **5** are best formulated to possess two Ph₃E⁻ groups formally bound to d⁸ Ir(I) moieties. For comparison, the more electron rich four-coordinate tricarbonyliridate complex, [Ir(CO)₃(PPh₃)]⁻, which formally contains d¹⁰ Ir(I−), exhibits IR ν(CO) values of 1840 and 1860 cm⁻¹,[26] which are shifted 70−90 cm⁻¹ to lower energy than those of **4** and **5**.

Structural Characterizations of [(C₂H₅)₄N][Ir(CO)₃(EPh₃)₂], E = Sn (4), Ge (5), and [(C₂H₅)₄N][Co(CO)₃(SnPh₃)₂] (6). Salts **4**, **5**, and **6** crystallize in the space group *Cc* as colorless dichloromethane solvates and have very similar unit cells, but are not isomorphous. The asymmetric unit of each structure contains one tetraethylammonium cation, one *trans*-[M(CO)₃-(EPh₃)₂]⁻ unit, and one dichloromethane molecule. The tetraethylammonium cations and CH₂Cl₂ groups are ordered, are well separated from the anions, and show no unusual features. Interatomic data for the latter are available in the Supporting Information. Transition metals in the anions are in a nearly ideal trigonal bipyramidal environment. For example, the M(CO)₃ fragments are planar with all C−M−C angles close to 120°, and the E−M−E units are nearly linear, with angles ranging from 173 to 175°. The pyramidal triphenylstannyl and triphenylgermyl units in **4**, **5**, and **6** show no unusual features. Interatomic data for the latter are also available in the Supporting Information. Figure 1 shows the molecular structure of *trans*-[Ir(CO)₃(SnPh₃)₂]⁻. Selected interatomic data for the anions are listed in Table 2. Average Ir−C and C−O distances in **4** and **5** are well within the usual range of values previously observed for terminal carbonyl groups bound to low-valent iridium.[29−31] However, and as expected, these values are far different from
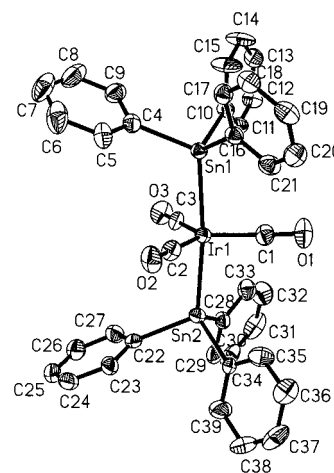
Figure 1. Molecular structure of *trans*-[Ir(CO)₃(SnPh₃)₂]⁻ (50% thermal ellipsoids); hydrogens are omitted for clarity. See Table 2 for selected bond distances and angles.

Table 2. Selected Bond Distances (Å) and Angles (deg) for *trans*-[M(CO)₃(EPh₃)₂]¹⁻ in **4**, **5** and **6**

compd, M/E	**4**, Ir/Sn	**5**, Ir/Ge	**6**, Co/Sn
M−C(1)	1.882(6)	1.893(7)	1.756(5)
M−C(2)	1.891(6)	1.894(6)	1.748(5)
M−C(3)	1.883(5)	1.899(7)	1.741(5)
M−C (av)	1.885(6)	1.895(7)	1.748(8)
C(1)−O(1)	1.180(7)	1.161(8)	1.155(5)
C(2)−O(2)	1.135(7)	1.135(7)	1.161(5)
C(3)−O(3)	1.164(6)	1.117(7)	1.162(5)
C−O (av)	1.16(2)	1.14(2)	1.159(5)
M−E(1)	2.6284(4)	2.4922(8)	2.4906(8)
M−E(2)	2.6289(4)	2.4932(8)	2.4889(8)
E−C(Ph) (av)	2.17(1)	1.984(8)	2.169(5)
M−C(1)−O(1)	177.5(6)	178.6(7)	179.6(4)
M−C(2)−O(2)	178.2(6)	179.4(7)	179.8(5)
M−C(3)−O(3)	178.2(5)	177.5(6)	178.9(5)
M−C−O (av)	178.0(6)	178.5(9)	179.4(5)
C(1)−M−C(2)	118.5(2)	119.7(2)	119.7(2)
C(1)−M−C(3)	117.5(2)	118.1(3)	116.9(2)
C(2)−M−C(3)	124.0(2)	122.2(3)	123.5(2)
C−M−C (av)	120(4)	120(3)	120(3)
E(1)−M−E(2)	173.47(1)	175.05(3)	174.39(3)
C(1)−M−E(1)	92.0(2)	91.2(2)	92.1(2)
C(2)−M−E(1)	87.6(2)	88.9(2)	87.9(1)
C(3)−M−E(1)	90.1(2)	89.9(2)	90.1(1)
C(1)−M−E(2)	94.4(2)	93.5(2)	93.5(2)
C(2)−M−E(2)	90.2(2)	90.1(2)	90.1(1)
C(3)−M−E(2)	85.9(2)	86.5(2)	86.7(1)
C−M−E (av)	90(3)	90(2)	90(3)

the average Ir−C and C−O distances of 2.02(2) and 1.08(2) Å, respectively, found in [Ir(CO)₅Cl]²⁺, in which the CO groups are believed to function as essentially pure σ-donors to the strongly electrophilic d⁶ Ir(III) center.[32,33]

The observed average Ir−Sn distance of 2.6286(4) Å in **4** is unexceptional in comparison to corresponding values previously reported for other triphenyltin iridium complexes. For example, the shortest and longest such distances were in the d⁴ Ir(V) complex, (C₅Me₅)Ir(H)₃(SnPh₃), 2.588 (1) Å,[34] and the previously mentioned d⁸ Ir(I) species, Ir(CO)₃(PCy₃)(SnPh₃), 2.6610-

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(3) Å,[30] respectively. To the best of our knowledge, no prior examples of triphenylgermyl iridium complexes have been structurally characterized, but the reported Ir−Ge distance of 2.484(2) Å in the trimethylgermyl Ir(III) species, $Ir(CO)(H)_2$-$(PPh_3)_2(GeMe_3)$,[35] is only slightly shorter than the average Ge−Ir distance of 2.4927(8) Å determined for **5**. Two other molecules containing Ir−Ge bonds have been structurally characterized, but they contain $Ge(N(SiMe_3)_2)_2$ or related ligands[36] that are sufficiently different sterically and electronically from simple trialkyl- or triarylgermyl units that comparisons of the Ge−Ir distances, which range from 2.325(3) to 2.466(2) Å, with those in **5** are not of any relevance to this discussion. In conclusion, the structural data for the anions in **4** and **5** corroborate our prior formulations, based on elemental analyses and solution spectroscopic data. Also, the interatomic data for **4** and **5** appear to be entirely normal compared to those of previously known mixed tin−iridium carbonyls, germanium−iridium carbonyls, and related species.

To help confirm our prior claims on the formulation of $[Co(CO)_3(SnPh_3)_2]^-$ [10,20] and to provide additional evidence that the carbonylcobaltate(3−) precursor, $Na_3[Co(CO)_3]$, is indeed a tricarbonyl complex, a structural characterization of **6** was carried out. The basic architecture of the *trans*-[Co(CO)_3-$(SnPh_3)_2]^-$ units in **6** has been described earlier in the paper. This section will provide details on important interatomic distances. The average Co−C and C−O distances in **6**, see Table 2, are unexceptional compared to corresponding values previously established for tricarbonylcobalt(I) complexes.[31] The latter include the *trans*-trigonal bipyramidal complexes $Co(CO)_3$-$(PPh_3)(GePh_3)$,[37] $[Co(CO)_3(SnCl_3)_2]^-$ (**7**),[38] $Co(CO)_3(PPh_3)$-$(SnMe_3)$ (**8**),[39] and $Co(CO)_3(AsPh_3)(SnMe_3)$ (**9**).[39] The average Co−Sn distance of 2.4898(8) Å in **6** is somewhat longer than those reported for **7**, 2.442(2) Å, which was described as being "remarkably short",[38] and $Co(CO)_4SnCl_3$, 2.477(1) Å,[40] but is significantly shorter than the Co−Sn distances found in **8**, 2.574-(2) Å, and **9**, 2.565(1) Å.[39] All previously reported structures containing triphenylstannyl−cobalt units have appreciably longer Co−Sn distances than those in **6**, including $Co(\eta^4$-anthracene)(PMe_3)_2(SnPh_3)$,[25f] 2.546(2) Å, and $Co(PMe_3)_3$-$(SnPh_3)$, 2.590(2)−2.598(2) Å,[24a] for three independent molecules in the unit cell. Very likely the triphenylstannyl units in

6 are able to approach the Co(I) center more closely for both steric and electronic reasons; i.e., CO ligands are both smaller and much better acceptors than the PMe_3/anthracene units present in the above mixed $Co(PMe_3)_x(SnPh_3)$ species.[24a,25f]

Concluding Remarks

Reduction of $Na[Ir(CO)_4]$ by sodium in hexamethylphosphoramide (HMPA) generates soluble $Na_3[Ir(CO)_3]$. Treatment of this solution with excess liquid ammonia results in the precipitation of high yields, ca. 90%, of a pyrophoric orange solid, which proved to be satisfactorily pure unsolvated Na_3-$[Ir(CO)_3]$. The latter is of interest as the only substance to contain Ir(III−), the lowest known formal oxidation state of iridium. IR spectra for this unusually electron rich carbonylmetalate show a carbonyl stretching mode at very low energy, ca. 1665 cm^{-1}, indicating that the metal−CO bonding in this species involves substantial metal π donation to the carbonyl groups. In contrast, the previously reported Ir(III) complex, $[Ir(CO)_6]^{3+}$, has an IR $\nu(CO)$ value of 2254 cm^{-1}, sufficiently far above that of gaseous CO, 2143 cm^{-1}, that the metal−CO bonding is believed to involve only carbonyl σ donation to the metal center.[32] Thus, in proceeding from $Na_3[Ir(CO)_3]$ to $[Ir(CO)_6][Sb_2F_{11}]_3$[32] the IR $\nu(CO)$ value increases by nearly 600 cm^{-1}! This may well be the largest span of $\nu(CO)$ values known for terminal CO groups in homoleptic complexes of any given metal.

Interactions of $Na_3[Ir(CO)_3]$ with Ph_3ECl, E = Sn, Ge, provided the respective mixed main group−transition metal species *trans*-$[Ir(CO)_3(EPh_3)_2]^-$, the first five-coordinate anionic iridium carbonyls. Beck and co-workers have also obtained the unusual mixed rhenium−iridium hydride, $(OC)_5Re−Ir(CO)_3H−Re(CO)_5$, by the reaction of $Na_3[Ir(CO)_3]$ with the highly reactive cationic carbonyl, $[(\eta^2\text{-}C_2H_4)Re(CO)_5]^+ PF_6^-$.[40] To the best of our knowledge, our present study and that of the Beck group report on the only known reactions of $Na_3[Ir(CO)_3]$. However, these few examples suggest that the carbonyliridate-(3−) should have a rich chemistry and be a useful precursor to new classes of mixed main group element− and/or transition metal−iridium carbonyl complexes.

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