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IRIDIUM ATOM CHEMISTRY: A REAPPRAISAL OF THE MATRIX SYNTHESIS OF DIIRIDIUM OCTACARBONYL, $Ir_2(CO)_8$

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Summary

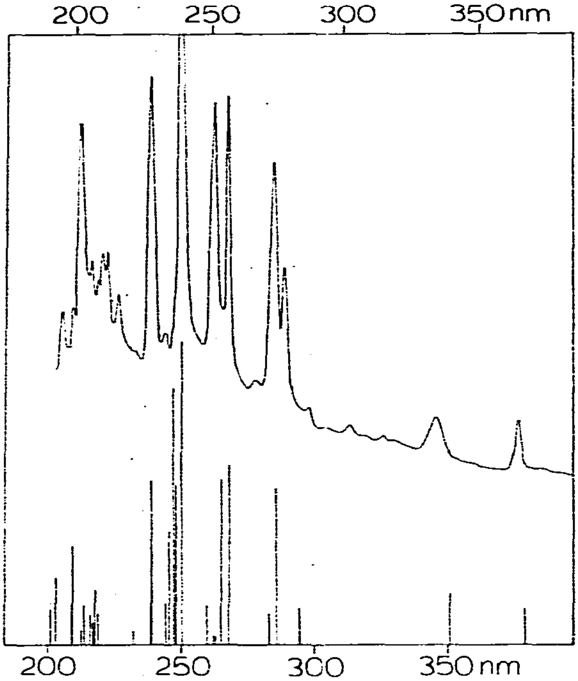
Matrix entrapped iridium atoms are investigated in solid Ar, Kr and Xe at 10—12 K for the first time. An impressive correlation between the multitude of atomic resonance lines in the gas and matrix phases is observed for ground state Ir $5d^76s^2$ ($^4F_{9/2}$). A search for naked diiridium or higher clusters in these matrices proved to be fruitless. A recently unveiled suppliers error in our original publication of purported $Ir_2(CO)_8$ (rhodium metal confused for iridium) necessitated a reinvestigation and reappraisal of the products of Ir/CO matrix co-condensations at 10—12 K. These reactions are shown in this study to yield authentic samples or $Ir(CO)_4$ and its dimerization product $Ir_2(CO)_8$. Unlike $Rh_2(CO)_8$, the latter species is found to exist as the metal—metal bonded, non-bridged isomer (analogous to non-bridged $Co_2(CO)_8$) and around 200 K undergoes what appears to be decomposition to quite large iridium clusters onto which CO is chemisorbed, rather than to a well defined disproportionation product such as $Ir_4(CO)_{12}$.

Other than a brief report of a probable Ir atomic band observed by Jansson and Scullman [1] in an investigation of the matrix spectrum of IrO and the purported matrix synthesis by Hanlan and Ozin [2] of $Ir_2(CO)_8$, there has been essentially no other cryochemical research into either the spectroscopy of naked atomic iridium and its higher clusters or the chemistry of iridium vapor and its cluster complexes. In this brief report we wish to present results of the first detailed study of atomic iridium isolated in solid Ar, Kr and Xe. Furthermore, we wish to correct an unfortunate error in our original report of $Ir_2(CO)_8$, which because of an unsuspected suppliers oversight (rhodium for iridium metal) and a subtle infrared spectral disguise, was unfortunately confused with an authentic sample of $Rh_2(CO)_8$ and thereby misassigned [2]. Employing a "real" sample of iridium metal, we can now report with confidence that

$Ir(CO)_4$ is indeed the major product of Ir/CO $\simeq 1/10^4$ to $1/10^2$ co-condensations at 10—12 K and can be subsequently induced to dimerize in CO around 30—40 K, or on gradually subliming off the CO matrix around 50 K, to yield the *non-bridged isomer* of $Ir_2(CO)_8$. Let us first consider the optical data for iridium vapor co-condensed with weakly interacting inert gas matrices, thereby establishing the conditions necessary for isolating atomic iridium. This will then be followed by an infrared investigation of the products generated in 10—12 K co-condensations of iridium vapor and carbon monoxide.

Iridium vapor—inert gas condensations

Since a number of previous investigations have indicated that the extent of metal diatomic and higher cluster formation on co-condensing metal atomic vapors with weakly interacting supports at low temperatures is strongly affected by the matrix surface diffusion processes that occur during deposition, it might be expected that the heaviest element of the cobalt group would display the least tendency towards cluster formation. Our experiences so far with iridium indicate this to be the case. However, we should point out that iridium atom aggregation experiments are complicated by the extremely high



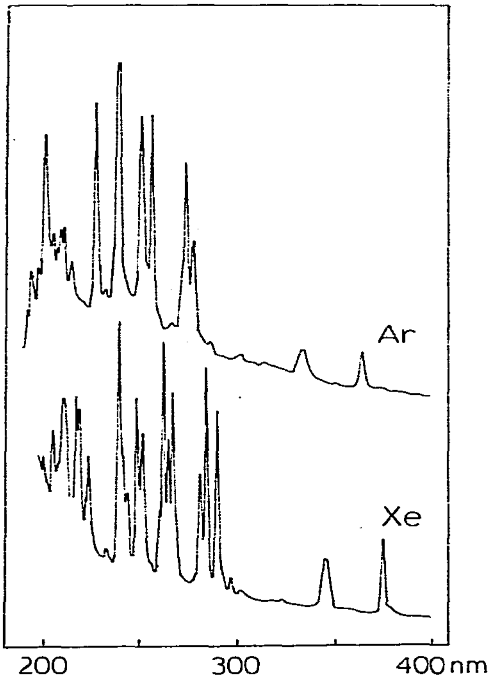


Fig. 1. The optical spectrum of Ir atoms isolated in solid Ar at 10—12 K compared to the gas phase atomic transitions of Ir. The stick heights correspond to reported oscillator strengths [3] of gaseous Ir atoms.

Fig. 2. Correlation of the optical spectra of Ir atoms isolated in Ar and Xe matrices under identical conditions of temperature (10—12 K) and metal and gas deposition rates (metal/inert gas $\simeq 1/10^4$).

temperatures required to achieve iridium vaporization and the difficulties therefore of establishing reproducible metal deposition conditions, a prerequisite for quantitative iridium atom-matrix concentration experiments.

Deposition of iridium vapor with argon at concentration ratios of roughly $1/10^4$ and at 10—12 K resulted in the optical spectrum shown in Fig. 1. Considering the plethora of sharp, well defined lines of matrix entrapped Ir com-

TABLE 1

THE OPTICAL SPECTRUM OF Ir ATOMS ISOLATED IN SOLID Ar AT 10—12 K COMPARED TO THE GAS PHASE FREE ATOM TRANSITIONS: GROUND STATE ELECTRONIC CONFIGURATION OF Ir $5d^7 6s^2$, $^4F_{9/2}$

Free atom; gas phase		Observed in solid argon 10—12 K		$\nu_M - \nu_G$ (cm^{-1})	Configuration	Designation [a]
nm	cm^{-1}	nm	cm^{-1}			
380.0	26,308	364	27,473	1165	$5d^7 6s6p$	$^6D^0_{9/2}$
351.4	28,452	334	29,940	1488	$5d^7 6s6p$	$^6F^0_{11/2}$
		314	31,847			
		301	33,223			
295.1	33,874	286	34,965	1091	$5d^7 6s6p$	$^6F^0_{7/2}$
284.9	35,081	277	36,101	1020	$5d^7 6s6p$	$^6G^0_{9/2}$
282.3	35,411	273	36,630	1219	$5d^7 6s6p$	$^6G^0_{7/2}$
		267	37,453			
266.5	37,512	256	39,063		$5d^7 6s6p$	$^4D^0_{7/2}$
263.9	37,872				$5d^7 6s6p$	$^4F^0_{9/2}$
261.9	38,158	251	39,841		$5d^7 6s6p$	$^4F^0_{7/2}$
261.5	38,230					
259.2	38,568					
250.3	39,940	240	41,667			
248.1	40,291					
247.5	40,390					
245.6	40,711					
243.1	41,119	232	43,103	1984		
237.3	42,132	228	43,860	1728		
231.5	43,176	221	45,249	2073		
217.8	45,896	215	46,512	616		
217.5	45,957					
216.3	46,220	211	47,393	1173		
215.6	46,372	209	47,847	1475		
212.8	46,979	207	48,309	1330		
211.9	47,165	205	48,781	1616		
208.9	47,858	201	49,751	1893		
203.4	49,159	198	50,505	1346		
201.1	49,719	195	51,282	1563		

[a] Designations from 243—201 nm not assigned in ref. 4.

pared to those of Co and Rh, one observes a remarkably impressive correlation with the representation of the atomic gas phase emission spectrum as reported by Gruen [3] and Moore [4]. Table 1 more accurately compares each matrix absorption with that of the gas phase and lists the corresponding term assignments, where known. From this comparison, weak features in the 300—340 nm region of the argon matrix spectrum were found to have no corresponding gas phase emission bands.

In an attempt to further investigate those weak spectral features which might be due to diatomic or higher iridium clusters, the optical spectrum of Ir vapor was examined in Ar, Kr and Xe matrices under identical deposition conditions. The observed transitions of atomic iridium in the three matrix materials are compared in Table 2 while Fig. 2 illustrates the correlation of the spectra in argon and xenon. The most notable difference in the two spectra observed in argon and xenon matrices, besides the expected red shift, was the transformation of the two sets of doublets observed in Ar at 277/273 nm and 256/251 nm to triplets at 289/284/281 nm and 267/264/262 nm in xenon matrices. In addition, the single atomic transition at 240 nm in argon became a lower intensity doublet at 252/248 nm in xenon. Such an observation of additional band splitting on changing from one matrix material to another has been previously observed and attributed to changes in the spin orbit coupling interactions [5] and crystal field effects [6]. Such effects can result in changes in the magnitude of the splitting of degenerate energy levels [7]. Complete understanding of these matrix effects has not yet been achieved.

Other than the additional band splittings, referred to above, the spectra of iridium vapor deposited with Ar, Xe matrices basically show the same atomic features, with each band in Ar having a counterpart in Xe; this also includes those observed in the 300—340 nm region in Ar. From this it can be stated that under the deposition conditions employed, detectable amounts of diiridium were not formed in argon, where diffusion—aggregation events are expected to be most pronounced. Quantitative iridium concentration studies may reveal new bands, at higher iridium/matrix ratios or higher temperatures, assignable to few-atom iridium clusters. We note here that ground state iridium atoms (electronic configuration $5d^7 6s^2$) may require a considerably higher matrix deposition temperature than 10—12 K to facilitate dimerization and higher clustering events, in view of larger activation energies to diffusion (mass effect) and/or valence state promotion (ground state atomic Rh has the electronic configuration $4d^8 5s^1$) compared to the lighter congeners of the cobalt group.

Iridium vapor—carbon monoxide co-condensations

With the success of the metal atom-matrix preparations of $Co_2(CO)_8$ [9] and a bridge bonded form of $Rh_2(CO)_8$ [2], our next step was to apply the technique to iridium in a designed effort to complete the cobalt triad with formation of $Ir_2(CO)_8$. At this point it is necessary to withdraw our initial report of the metal atom synthesis of $Ir_2(CO)_8$ as it appeared in ref. 2. Results obtained with Ir at that time bore a disquieting resemblance to those of Rh. Subsequent X-ray fluorescence analysis revealed that the metal, supplied to us as Ir by Imperial

Smelting via Johnson Mathey, was in fact Rh [*].

With an authentic sample of Ir (supplied by McKay of N.Y. and verified by analysis), the iridium atom—carbon monoxide matrix reactions have now been repeated, using conditions designed to favor binuclear complex formation ($Ir/CO \simeq 1/10^2$ to $1/10^3$). Upon deposition at 10—12 K, $Ir(CO)_4$ (identified and characterized in detail ($^{12}C^{16}O/^{13}C^{16}O/^{13}C^{18}O/^{12}C^{18}O$ isotopic substitution experiments) in ref. 8) was still the major absorbing species (Fig. 3A, 3B) but in addition, three new, weak features were observed in the ν(CO) terminal bonding region at roughly 2065, 2052 and 2040 cm^{-1} (Fig. 3A, B). On carefully warming the matrix in the range 30—40 K the three new bands gradually increased in intensity (Fig. 3C, D) accompanied by a slight shift in their frequencies with a concomitant decrease in the intensity of the $Ir(CO)_4$ species. Such behaviour was reminiscent of the dimerization process observed for both $2\ Co(CO)_4 \rightarrow Co_2(CO)_8$ [9] and $2\ Rh(CO)_4 \rightarrow Rh_2(CO)_8$ [2] and strongly suggests that an analogous mechanism was operative for $Ir(CO)_4$. It should be noted that at no time, either after decomposition or on warming, was any evidence found for new absorptions in the ν(CO) bridge bonding region (1800—1900 cm^{-1}) of the spectrum (cf. $Co_2(CO)_8$ and $Rh_2(CO)_8$). Comparison of the new ν(CO) bands with the non-bridged, metal—metal bonded isomer of $Co_2(CO)_8$ (Table 3) provided strong evidence that a similar non-bridged $Ir_2(CO)_8$ complex had formed in the matrix. That this species should appear in a non-bridged form (cf. $Rh_2(CO)_8$ bridged form under comparable conditions) was not unexpected as the tendency for formation of bridged carbonyl complexes decreases on transcending a group, as the metal atom gets larger and metal—metal bond strengths increase [11]. This trend is reflected in the structures of the $M_4(CO)_{12}$ complexes, where both the Co and Rh analogues contain terminal and bridging CO groups [12,13], whereas the ligand bonding in the Ir cluster is exclusively terminal [12].

To further investigate the purported dimerization reaction of $Ir(CO)_4$ to $Ir_2(CO)_8$ and any subsequent decomposition/disproportionation reactions for the proposed $Ir_2(CO)_8$ complex, the CO matrix was warmed to 50 K and gradually pumped away from the remaining complex. At this point a slight variation in the method used in the study of $Rh_2(CO)_8$ [2] was employed. Once the CO matrix had sublimed from the sample remaining on the cold window at 50 K the reaction chamber and cold optical plate was isolated from the pumping system and the non-matrix isolated sample was cooled back down to 10—12 K; Fig. 3E illustrates the resulting spectrum. It can be seen that those bands attributed to $Ir(CO)_4$ have collapsed to zero leaving only a broad absorption band in the

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[*] On reviewing the earlier data (ref. 2) it appears that interpretive discrepancies mainly arose from too fast a matrix sublimation at too high a temperature (actually 75 K rather than 50 K as originally reported) for the purported sample of $Ir(CO)_4$ in solid CO (actually $Rh(CO)_4/CO$). Under these conditions, larger metal carbonyl clusters than originally anticipated seem to have been formed and the spectra reported in 1974 bear a striking resemblance to those of CO chemisorbed on quite large Rh_n aggregates. This proposal is strengthened by some bulk annealing data for Rh/CO matrices rich in rhodium metal. The spectral transformations which ensue on warming these matrices above 200 K appear to be associated with ligand rearrangements and/or metal nuclearity changes involving quite large Rh clusters. These effects occur fortuitously close to the —48° C range where authentic $Rh_2(CO)_8$ disproportionates to $Rh_4(CO)_{12}$ (ref. 2). Hence the originally reported —58° C decomposition temperature for purported $Ir_2(CO)_8$ is meaningless.

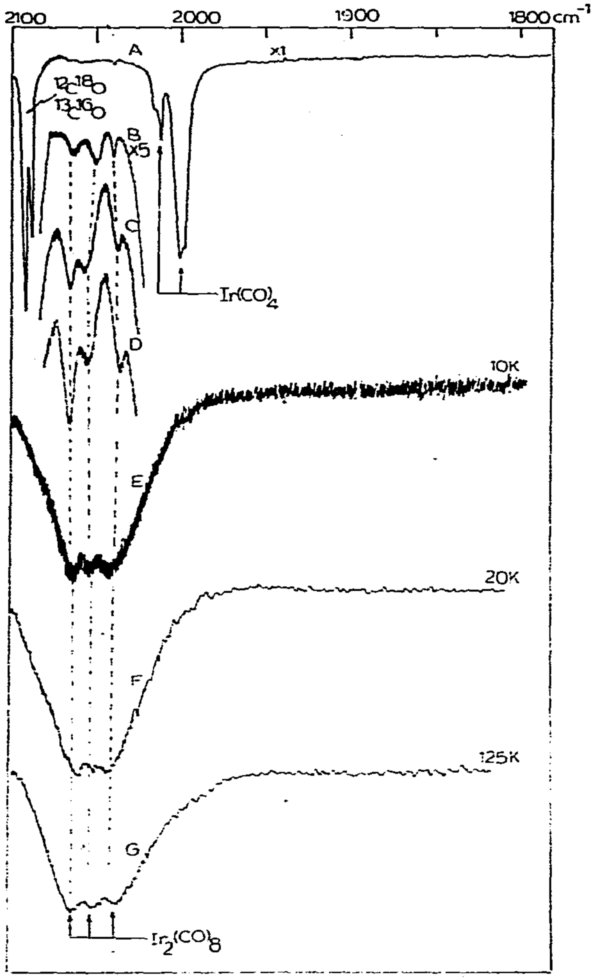

Fig. 3. The infrared spectrum of the products of the co-condensation reaction of iridium vapor with pure carbon monoxide ($^{12}C^{16}O$) at Ir/CO $\simeq 1/10^2$ (A) on deposition at 10—12 K showing mainly $Ir(CO)_4$, natural abundance $^{12}C^{18}O/^{13}C^{16}O$ and traces of $Ir_2(CO)_8$, the latter seen on 5X ordinate expansion of (A) as in (B); (C, D) the result of annealing the matrix shown in (A) at 30 and 40 K showing the decay of $Ir(CO)_4$ and growth of $Ir_2(CO)_8$; (E) the effect of subliming off the CO matrix at 50 K and recooling to 10—12 K showing non-isolated $Ir_2(CO)_8$ and (F, G) subsequent warming of $Ir_2(CO)_8$ at 20 K and 125 K.

2030—2070 cm^{-1} $\nu(CO_t)$ region; still clearly evident however, were the three bands assigned to $Ir_2(CO)_8$, slightly shifted to 2062, 2055 and 2040 cm^{-1} for the "non-matrix isolated complex" with respect to 2065, 2052 and 2040 cm^{-1} for $Ir_2(CO)_8$ entrapped in solid CO. Gradual warming of this sample to 125 K (Fig. 3F, G) produced very little change in the spectrum other than a slight shift in the frequencies. Further warming in the temperature range 150—200 K caused a gradual decrease in the intensity of the original triplet, concomitant broadening, leading eventually to a broad absorption centred at about 2060 cm^{-1}, which closely resembles the spectrum of CO chemisorbed on oxide supported Ir clusters [14].

During the course of these thermal stability tests from 10—12 K to room

TABLE 2

THE OPTICAL SPECTRA OF Ir ATOMS IN SOLID Ar, Kr AND Xe AT 10—12 K COMPARED TO THE GAS PHASE TRANSITIONS

Free atom; gas phase (nm)	Argon (nm)	Krypton (nm)	Xenon (nm)	Free atom; gas phase (nm)	Argon (nm)	Krypton (nm)	Xenon (nm)
380.0	364	368	374	248.1	240	242	252
351.4	334	336	345	247.5			248
	314		323	245.6			
	301		301	243.1	232		243
295.1	286		296	237.3	228	233	239
284.9	277	283	289	231.5	221		232
			284	217.8	215	219	224
282.3	273	277	281	217.5			222
	267			216.3	211	213	218
266.5	256	261	267	215.6	209		216
263.9			264	212.8	207		
261.9	251	256	262	211.9	205		215
261.5				208.9	201	205	210
259.2			259	203.4	198	199	205
250.3				201.1	195	195	201

temperature, no obvious evidence was obtained for the disproportionation reaction

$$2\ Ir_2(CO)_8 \rightarrow Ir_4(CO)_{12} + 4\ CO$$

as was observed in the corresponding Rh study [2]; however, it is not inconceivable that absorptions due to $Ir_4(CO)_{12}$ (Table 3) were hidden under the broad band enveloping the 1960—2100 cm^{-1} region.

Based on comparison with the corresponding metal atom syntheses of $Co_2(CO)_8$ [9] and $Rh_2(CO)_8$ [2] and by analogy to the metal—metal bonded $Co_2(CO)_8$ isomer, the new IR spectral features can be associated with the non-bridged form of $Ir_2(CO)_8$. A quantitative study of the formation of this complex as a function of the Ir/CO ratio would strengthen our proposals; however, to achieve this end a more controlled and reproducible technique for vaporizing Ir metal than that employed in the present study, will have to be developed [15].

Meanwhile, the infrared data for the iridium atom—carbon monoxide reac-

TABLE 3

COMPARISON OF THE INFRARED SPECTRA OF METAL—METAL BONDED $Co_2(CO)_8$, $Ir_2(CO)_8$ AND $Ir_4(CO)_{12}$ (cm^{-1})

$Co_2(CO)_8$ [a]	$Ir_2(CO)_8$ [b]	$Ir_4(CO)_{12}$ [c]	Assignment
		2073	$\nu(CO_t)$
2069	2065		$\nu(CO_t)$
2031	2052		$\nu(CO_t)$
2022	2040		$\nu(CO_t)$
		2032	$\nu(CO_t)$

[a] Non-bridged form ref. 10. [b] Recorded under dynamic vacuum (10^{-6} torr). [c] Ref. 11,12.

tions described in this brief report provide reasonably convincing interim evidence for the existence of $Ir_2(CO)_8$ formed from the matrix dimerization of the well established tetracarbonyl radical, $Ir(CO)_4$ [8]. The instability of $Ir_2(CO)_8$ with respect to a decomposition reaction around 200 K to higher (unidentified) iridium clusters, is certainly consistent with the difficulties encountered by various groups of organometallic chemists who have attempted to synthesize the "elusive" $Ir_2(CO)_8$ complex by conventional, room temperature preparative techniques [2].

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