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An Investigation of Possible Photolysis and Thermolysis Effects in Metal Atom Cocondensation Procedures. Crucible Insulation Effects on Metal Atom Oxidative Addition, Alkene Isomerization and Polymerization, and the Discovery of Homogeneous Metal-Polymer Solutions.

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Abstract

During metal atom cocondensation procedures, the metal vaporization sources operate about 1220-1800°C emitting a great deal of light. Insulation of these crucibles effectively cuts down heat and light emission, but also adds greatly to the surface area where thermolysis reactions may occur. The effect of crucible insulation has been studied in an oxidative addition reaction (Pd + $C_6H_5CH_2Cl$), alkene isomerization (Ni + alkenes), and alkenes polymerizations (Ni + styrene and tetrafluoroethylene). Our findings indicate that the effect of wool insulators (Kaowool or Fiberfrax) is not a photolytic effect, but a pyrolysis

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effect. This pyrolysis causes production of organic free radicals from the substrate, and these radicals cause destruction of $C_6H_5CH_2PdCl$, isomerization and polymerization of alkenes. No effects attributable to photolysis or matrix warming in the absence of insulator were found. Thus, the presence of wool insulators caused polymerization and isomerization reactions to be several fold greater in importance.

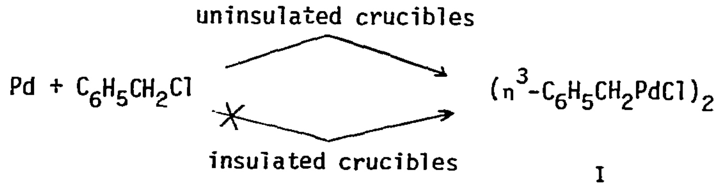
During the course of this work we discovered that homogeneous Ni-polystyrene solutions could be produced, and this has proven to be a selective nickel catalyst worthy of further study.

Introduction

With the maturation of the metal atom cocondensation technique[1] for the synthesis of novel metal-organic,[1c] and metal-inorganic[1b] complexes and catalysts,[2] the method has now been fairly widely accepted as a new approach to normal synthetic chemistry[1c,1d] as well as matrix isolation spectroscopy micro synthetic procedures.[1d] However, it must be realized that the technique involves some rather incredible experimental extremes. The metal vaporization sources, generally commercially available integral tungsten-aluminum oxide crucibles or tunsten boats, operate at 1000-1800°C, while the reaction to form the temperature sensitive products usually takes place about -100 to -190°C. The separation between these zones is usually about 2-4 inches. In addition, the vaporization sources emit a great deal of light that may affect photosensitive organometallic products. Of course the question arises as to whether the presence of this very hot, light emitting source affects reactions in any way, adversely or positively.

Under ideal conditions (excellent vacuum, direction of substrate stream, crucible shape, etc.) neither substrate nor product should contact the hot crucible, because of the long mean free path of metal atoms and substrate molecules. However, in practice this appears not be the case, and the degree of interaction of the substrate with the hot source probably will vary for each experiment, and will be dependent on the exact design of the apparatus, including the substrate inlet tube, vacuum, sticking coefficient of substrate molecules, products produced upon pyrolysis, rate of deposition, and perhaps other factors.

We became interested in this problem and in carrying out some investigations on the effects of hot crucible presence because of the finding of Professor Timms of Bristol University. Timms could not reproduce some of our work on the metal atom synthesis of the benyl-palladium chloride dimer.[3,4] Learning this, we immediately began a more in depth investigation of this synthetic procedure and found that in depth Timms employed insulated crucibles whereas in the original work, we had not. Thus, we began a broad investigation of the effects of



$$Pd + C_6H_5CH_2Cl \xrightarrow[\text{insulated crucibles}]{\text{uninsulated crucibles}} (\eta^3\text{-}C_6H_5CH_2PdCl)_2$$

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insulated vs. uninsulated crucibles. Our assumption was that either light or heat emitted from the source was causing the problem.

Results

I. Light Emission from Sources

First a study of the properties of emitted light from various metal vaporization sources was carried out. The sources were heated to an inside temperature of about 1450°C, the temperature at which Pd vaporization is moderately rapid. At this temperature a white to orange-white light is emitted. Through a pyrex metal atom reactor bottom, a Princeton Applied Research Optical Multichannel Analyzer (Mod 1205A fitted with a Jarrell-Ash 0.3M monochromator 22.6 nm/mm dispersion, 25μ slit) was employed to determine the wavelength of emitted light, and Figure I shows the intensity vs. wavelength scans for two sources. Figure I illustrates that the light emitted is a broad spectrum with λmax at 649 nm(A) and 620 nm (B), with the main emission in the 580 nm to 660 nm range. Note that essentially no

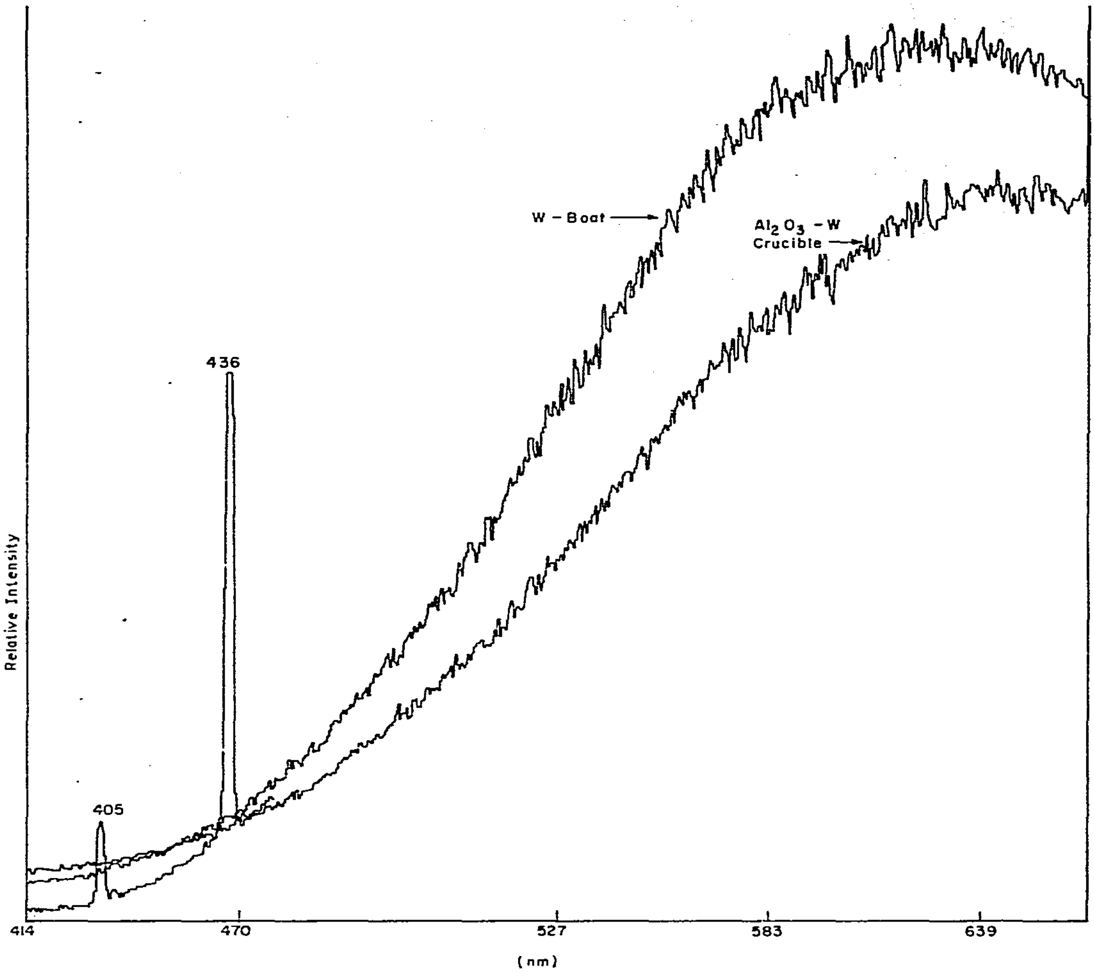


Figure 1

emission below 400 nm is observed (pyrex cutoff $\sim$ 300 nm). These results imply that almost no U.V. radiation is emitted, and that the highest intensity is in the visible near IR range. Also, the results show that although a broad radiation spectrum is emitted, as with black body radiation, these sources do not appear to follow ideal blackbody laws, since at 1450°C (1723°K) λ_{max} should be about 1680 nm.[5]

Although the sources do not behave exactly as blackbodies, the assumption that they approximate blackbodies well enough to allow calculations to be carried out yields some interesting further information concerning energy emitted in the U.V. range. Using the equation[6]

$$\text{total } E = I_T(\lambda)(d\lambda) = (C_1/\lambda^5)(1/(e^{C_2/\lambda T} - 1))\,d\lambda$$

$$C_1 = 3.7413 \times 10^{-5} \text{ erg cm}^2 \text{ sec}^{-1}$$

$$C_2 = 1.4388 \text{ cm deg}$$

with computer integration using either a trapezoidal rule or midpoint the formula method for the emission vs wavelength plot, the following total energies emitted for $d\lambda$ were found:

λ	200-400 nm	total E = 5.2×10^2 ergs/cm^2 sec
λ	400-600	1.8×10^4
λ	600-800	2.8×10^6
λ	800-1000	1.1×10^7
λ	1000-1200	2.1×10^7
λ	1200-1400	3.0×10^7
λ	1400-1600	3.5×10^7

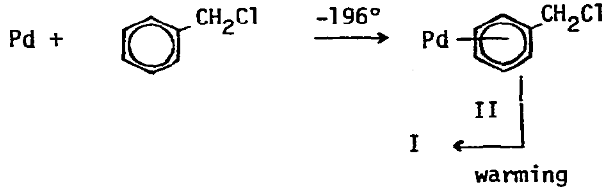
Overall total E = 9.9×10^7 ergs/cm^2 sec.

It should be noted that the U.V. range emits an almost negligible energy, while the visible emission is quite large. Of course, in the visible region, electronic is still the mode of excitation (30-80 Kcal/mole or $1.3\text{-}3.4 \times 10^{12}$ ergs/mole).

II. η^3-Benzylpalladium Chloride Dimer Formation[4]

Benzylchloride and palladium vapor were cocondensed employing different metal vaporization sources. The yield of η^3-benzylpalladium chloride dimer I (bis(η^3-benzyl di-μ-chloro-dipalladium)[4] was determined in each case. Table I summarizes the data and includes information concerning cocondensing temperature, and exposed luminescent surface of vaporization sources.

If a photoeffect beneficial to formation of product I is operating, we could make several observations at this point. Due to the very low U.V. output of the sources, and high visible output, the most likely photon active species would be a colored intermediate complex initially formed at low temperature between benzylchloride and Pd.[7] We observe



an initial red matrix at -196° which we believe is due to a π-complex(II) which converts to I on warming. Visible light could possibly interact with II to aid formation of I, and there is some slightly related literature precedent for this type of interaction. Kasai and McLeod[8] noted that long wavelength light was needed to induce a sodium atom electron transfer to B_2H_6. Similarly, Turner[9] found that an electron transfer from Na atoms and CO expulsion from $Cr(CO)_6$ was assisted by visible light.

$$Na_{atom} + B_2H_6/Ar \xrightarrow[\text{light}]{\text{long wavelength}} Na^+ B_2{}^-H_6$$

$$Na_{atom} + Cr(CO)_6/Ar \xrightarrow{h\nu(vis)} Cr(CO)_5{}^-$$

If light is beneficially interacting with II (dark red in color), then a dependence on yield of I vs area of luminescence of vaporization source would be expected. Figure II shows a plot of yield of I vs. exposed luminescence surface for each source in Experiments 1-10 of Table I. There appears to be no obvious correlation. In addition, there does not appear to be a correlation between total power input vs yield of I. In fact, the only apparent conclusion one can draw from Experiments 1-5 is that when an insulating wool is present, the reaction almost totally fails. When a Kaowool insulated crucible plus a non-insulated crucible are used together(Experiment 7), the reaction again failed. And the same results are found when the experiments are carried out at toluene slush temperature (-96°, Experiments 8-9 of Table I) instead of liquid nitrogen -196°C. In contrast, all other types of source shielding allowed the reaction to proceed to yield I (Experiments 4 and 6).

What is so deterimentally special about high special area wool insulation in that it is the only "ingredient" that causes the formation of I to fail? We considered this question and thereby developed a new set of questions that we attempted to answer: (1) Are impurities baked out of the wool (which is heated to ∿ 800-1400°C) during the codeposition that decompose I? Several blank experiments were carried out and the materials baked out of the Kaowool collected and analyzed. A small amount of water and a trace of ethane were found. Then prebaked (under vacuum) Kaowool was employed in the preparation of I, and again no product I was formed (Experiment 10 of Table I). (2) Can baked Kaowool cause the decomposition of I? A series of experiments were performed where Kaowool and prebaked Kaowool were allowed to contact I in benzyl chloride. No decomposition of I was found. (3) Can the presence of high surface area hot wool (Kaowool or Fiberfrax) cause pyrolysis of benzyl chloride as it is inletted, thus forming benzyl radicals which could strike the matrix and cause decomposition of I or II? If this were true, some toluene and bibenzyl formation would be expected, and the yields of these would be variable depending on Kaowool presence. Bibenzyl was not observed, but toluene was observed, and in considerably higher yield when Kaowool was present! In addition, blank experiments without Pd, yielded the same trend - more toluene when Kaowool was present. So toluene formation does come from pyrolysis of substrate, most likely through the intermediacy of $\phi\dot{C}H_2$, and the $\phi\dot{C}H_2$ formed obviously can destroy I (or prevent its formation by destruction of II) since the toluene yield is inversely proportional to the final yield of I.

Thus, it seems likely that the presence of the hot SiO_2-Al_2O_3 wool allows for efficient pyrolysis reactions of substrate, thereby causing formation of radicals that in turn cause the formation of I to fail. This is supported by the observation that the wool is always black at the end of an experiment, implying some pyrolysis of organics to form carbon. The reason that the wool is more effective than a hot crucible (no wool) must be due simply to the much greater available

(continued on p. 100)

Table I - Yields of η^3-Benzylpalladium chloride Dimer (I) vs Metal Vaporization Sources and Cocondensation Tempreature

Exp.	Source[a]	Amps	Volts	Luminescent Surface[b] (cm^2)	Source appearance during experiment	Cocondensation Temp. (°C)	Yield (% based on Pd vaporized)	Yield Toluene
(1)	Al_2O_3-W[c] no insulation (A)	45	5.5	5.8	outside orange-white, inside white	-196	15[d]	16
(2)	Al_2O_3-W[c] Kaowool insulation[e] (B)	24	5.2	1.8	outside not luminous, inside white	-196	1[f]	26
(3)	Al_2O_3-W[c] fiberfrax insulation[g] (C)	25	5	1.8	outside not luminous, inside white	-196	0.2	---
(4)	Al_2O_3-W[c] cylindrical steel (D) shield[h]	34	5.5	2.0	outside orange white but shielded from wall, inside white	-196	18	---
(5)	W boat[i] (E) no insulation	175	2.7	6.0	outside and inside orange-white	-196	16	---
(6)	Al_2O_3 crucible in shielded W heater[j] (F)	265	3.5	<0.5	almost no light emission at all	-196	14.2	---
(7)	A + B[k]	---	---	7.6	great deal of white light	-196	trace	---
(8)	B	25	5	1.8	cf. Exp. 2	-96	trace	---
(9)	E	175	2.7	6.0	cf. Exp. 5	-96	23	---

(10)	B with prebaked Kaowool	24	5.0	1.8	cf. Exp. 2	-196	0	---
(11)	A but no Pd	50	5.5	5.8	cf. Exp. 1	-196	---	8[l]
(12)	B but no Pd	25	60	1.8	cf. Exp. 2	-196	---	17[l]

(a) *cf*. Experimental section for more detail and vaporization source catalogs.

(b) Simple cyclindrial cone area calculations with critical judgements as to area exposed to reaction zone on reactor wall.

(c) Sylvania Emissive Products CS-1008 (cf. Exp. Section)

(d) Average of five experiments (all in 12-17% range)

(e) SiO_2-Al_2O_3 wool (*cf*. Exp. section)

(f) Average of four experiments (all in 1-2% range)

(g) SiO_2-Al_2O_3 wool (*cf*. Experimental Section)

(h) *cf*. Experimental Section

(i) Mathis Co. S-16 0.010 w (*cf*. Experimental Section)

(j) Mathis Heater B-19

(k) A special reactor with four electrodes employed. One empty source (B) and one Pd loaded source (A) were operated in tandem while benzyl chloride was inletted.

(l) Yield based on an assumed average amount of Pd that would have been vaporized under these conditions. The Kaowool experiment (experiment 13) yielded a large amount of polymer and orange solid, whereas the no-Kaowool experiment (experiment 12) did not.

hot surface area, and perhaps then the great availability of active SiO_2-Al_2O_3 sites for pyrolysis processes.

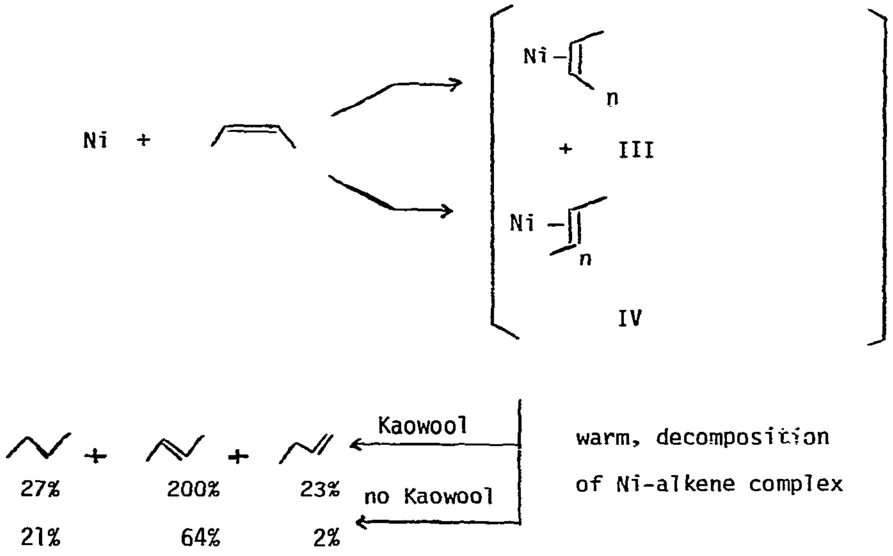
The fact that the matrix remains red during codeposition of benzyl chloride and Pd whether wool is present or not, probably indicates that the destruction of II (or I) by benzyl radicals does not take place until warmup (the time that we believe II goes to I). Thus, benzyl radicals (and Cl as well) are probably long lived in the low temperature matrix. And predictably the experiments at -96° when wool was present did not yield a red matrix during reaction; i.e., $C_6H_5CH_2\cdot$ reacted with II (or I) during deposition since -96° is a high enough temperature to allow radical abstraction reactions by $C_6H_5CH_2\cdot$ to proceed continually. A red-yellow matrix did form at -96° when wool was not present as insulator (Experiment 9, Table I).

III. Alkene Isomerization Reactions

To "load the case" so that low energy photons could cause reaction differences, we sought reactions where M-organic complexes initially formed would be light sensitive. Recent literature has shown that -196°C metal atom-alkene codepositions form M-alkene complexes efficiently.[10-13] Furthermore, the literature shows that M-alkene photochemistry is of great interest and that some M-alkene complexes are photosensitive toward alkene isomerization (double bond migration[14] cis-trans isomerization,[14] and dimerizations[15]).

We believed that by codepositing metal vapor and alkenes with or without crucible insulation, greater isomerizations would take place when insulation was absent (more light energy available). To our initial surprise the opposite effect was found! Thus, when Ni-cis-2-butene matrices were prepared with Kaowool crucible insulation and without Kaowool insulation, 200% and 64% isomerization were found respectively (based on Pd vaporized).

These experiments clearly dicate against any photolytic effect mechanism for the isomerization. However, a radical isomerization

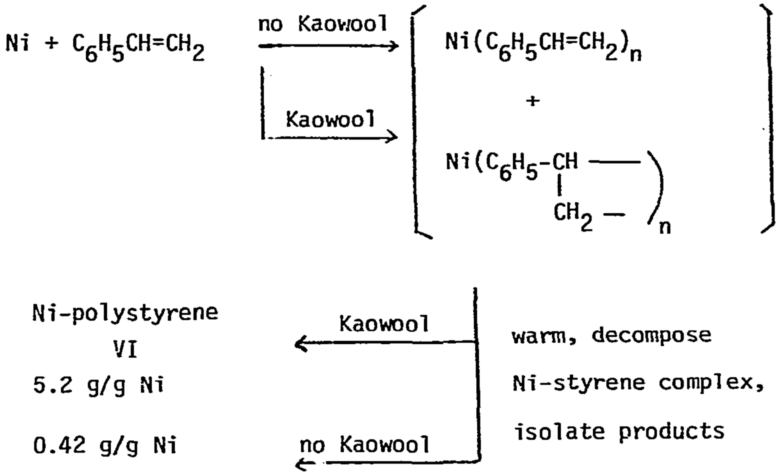


process is possible, considering that more radicals may be formed in the presence of Kaowool than in its absence, due to high surface pyrolysis effects. As in previous studies, pyrolysis evidence was present as the initially white Kaowool was black on the outer layers after completion of each experiment.

IV. Polymerization Processes - Styrene and Tetrafluoroethylene

It is known that Ni-styrene depositions yield metal complexes[16] and these could be photosensitive to polymerization. When we codeposited Ni vapor and styrene with or without Kaowool presence, we found *much less polymer formation in the absence* of Kaowool. Again, these results dictate against a photoytic mechanism, and strongly support a pyrolysis-radical process.

Analogous results were found for Ni-tetrafluoroethylene matrices, *i.e.*, with Kaowool 4.2 g polytetrafluoroethylene/g Ni vaporized and without 0.13 g polytetrafluoroethylene/g Ni vaporized was found.



VI. Ni-Polystyrene Metal Particle Dispersion

The Ni-polystyrene adduct, prepared successfully only in the presence of Kaowool, has some very interesting properties. It is a black solid totally soluble in toluene, but only slightly soluble in acetone. It appears to be air stable, and it serves as a selective homogeneous hydrogenation catalyst.

Currently we are investigating the production of other M-polystyrene adducts. Hopefully this procedure will be wide in scope for the production of homogeneous catalysts, and will compliment the procedures of Hirai, Nakao, and Toshima for preparing hydroxy functionalized M-polymer solutions.[17]

Conclusions

The generation of free radicals at least in small amounts, by substrate pyrolysis during metal vapor-substrate codepositions is unavoidable. The production of these radicals is greatly increased by the presence of high surface SiO_2-Al_2O_3 wool crucible insulator, and large concentrations of radicals so produced can have profound effects on synthetic reactions. Thus, $C_6H_5CH_2PdCl$ dimer formation can be prevented, olefins can be rapidly isomerized, and styrene and tetrafluoroethylene can be polymerized, all much more effectively in the presence of Kaowool insulator.

Experimental

Metal atom (vapor) cocondensation reactors we employ have been described before.[18] The metal vaporization sources listed in Table I are described in detail by their manufacturers[19] and in a recent review.[20] Briefly, W-Al_2O_3 crucible CS-1008 is a 1/2 cc volume conical W crucible with a fused coating of Al_2O_3 so that the cone will contain molten metal. Kaowool or Fiberfrax one cm thick was wrapped completely around the cone and attached with small nichrome wires on each side. Tungsten boats (Mathis S-16) are 0.010 inch thickness in the shape of a folded flat piece of metal with the ends crimped together. The W shielded heater is shaped like a box with end flaps for connection to the electrodes and with a round hole in the middle to contain a Al_2O_3 bucket-type crucible.

The insulation materials employed are also described in some detail by the suppliers. Kaowool[21a] is a stable, high temperature ceramic fiber, mp. 1760°C, fiber diameter ∿ 2.8 microns, chemical analysis: Al_2O_3 45%, SiO_2 52%, Fe_2O_3 1.3%, TiO_2 1.7% and traces of MgO, CaO, Na_2O and B_2O_3. No organic binders are used. Fiberfrax[21b] wool is supplied by Carborundum and is similar in makeup to Kaowool, although we do not know the exact composition. The cylindrical steel shield employed (Experiment 4, Table I) was fabricated from a 8 cm piece of 3 cm I.D. iron pipe with a 2 cm x 3 cm square hole cut on the top (for metal vapor exit from crucible) and a piece of metal rod welded on one end to serve as a support (connected to one electrode).

Experiments

General metal atom cocondensation procedures have been previously described.[1,4,20,22,23,24]

Nickel Vapor with *cis*-2-Butene (no insulation)

From a gas bulb, 51 mmoles of *cis*-2-butene was cocondensed with 0.28 g Ni (4.7 mg-atom) which yielded a brown matrix that turned black upon warmup. Volatiles were analyzed by glpc on a 25 foot HMPA column operating at 25C. There was a loss of 0.9 mmoles starting material during the reaction (due to pyrolysis, polymerization, etc.).

Nickel Vapor with cis-2-Butene (with Kaowool)

In this experiment 44 mmoles cis-2-butene were codeposited with 0.37 g·Ni (6.4 mg-atom) yielding a brown matrix. There was a loss of 2.2 mmoles starting material during the reaction (due to pyrolysis, polymerization, etc.).

Nickel Vapor with Styrene (no insulation)

Styrene (22 g, 24 ml, 200 mmoles) was codeposited with 0.347 g Ni (5.9 mg-atoms) in 1 hr - 20 min. The matrix was red-brown at low temperature and turned black near room temperature. A loss of 0.28 g (2.7 mmoles) occurred during the reaction. A clear polymer was formed (0.15 g).

Nickel Vapor with Styrene (with Kaowool)

Styrene (17.5 g, 19.3 ml, 170 mmoles) was codeposited with 0.362 g Ni (6.2 mg-atom) in a 1 hour - 30 minute reaction giving a red-brown matrix and a black solution at room temperature. A loss of 1.73 g (16.6 mmoles) styrene occurred during the reaction and 1.89 g of a black soluble polymer was isolated.

Nickel Vapor with Tetrafluoroethylene (no insulation)

From a gas bulb, 54.7 mmoles tetrafluoroethylene was codeposited in 30 minutes with 0.089 g Ni (1.5 mg-atom). A brown matrix formed which turned black on warming. Volatiles were collected and 53.2 mmoles were recovered, so that 1.5 mmoles starting material was lost to pyrolysis and polymerization. The reactor residue was washed twice with 15 ml portions of acetone, the solution filtered, and the acetone removed under vacuum leaving 0.0118 g polytetrafluoroethylene.

Nickel Vapor with Tetrafluoroethylene (with Kaowool)

As described in the previous experiment, 56.1 mmoles tetrafluoroethylene was cocondensed with 0.045 g Ni (0.77 g-atom). The yield of clear liquid polymer was 0.194 g. Glpc analysis of recovered starting material showed only one peak. (Hexamethylphosphorictriamide - 25' x 1/4" at 0° C).

Palladium Vapor with Benzyl Chloride

Table I describes the different experiments performed. The experimental procedures for preparing and isolating the η^3-benzylpalladium chloride dimer have been described previously.[4] In this work when toluene analysis was also desired, it was carried out by glpc analysis of volatile products plus starting material on a 10' 25% SE-30 column operating at 80°C.

Blank Experiments

Several experiments were carried out where no metal was loaded into the crucible. Reaction times, work up procedures, etc. remained the same as for the real experiments.

Sometimes Kaowool was prebaked by heating the crucible wrapped in Kaowool at metal vaporization temperature for a typical reaction time (eg. 1 hour). Any impurities baked out were removed, and then metal was loaded and the experiment carried out.

Acknowledgements

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