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PHOTOCHEMICAL AND THERMAL REACTIONS OF η^5 -CYCLOPENTADIENYL TETRACARBONYLVANADIUM AND BIS(PENTAFLUOROPHENYL)ACETYLENE

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Summary

The photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ in the presence of one or two equivalents of bis(pentafluorophenyl)acetylene yields $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$. One carbon monoxide ligand in this acetylene adduct can be photochemically displaced by triphenylphosphine to yield $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3](\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$. This complex is also obtained by the photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ in the presence of bis(pentafluorophenyl)acetylene. In vacuo, melt-phase thermolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$ and bis(pentafluorophenyl)acetylene produces $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$. This diacetylenic complex as well as the perfluorinated organic compounds 2,3,5,6-tetrakis(pentafluorophenyl)-1,4-benzoquinone, 2,3,4,5-tetrakis(pentafluorophenyl)cyclopentadienone and 2,3,4,5,6,7-hexakis(pentafluorophenyl)cycloheptatrienone are also obtained from thermal reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and bis(pentafluorophenyl)acetylene in solution. Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ in the presence of carbon monoxide produces $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$. The photochemical and thermal reactions of bis(pentafluorophenyl)acetylene and $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ are compared and contrasted with similar reactions of diphenylacetylene and $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$.

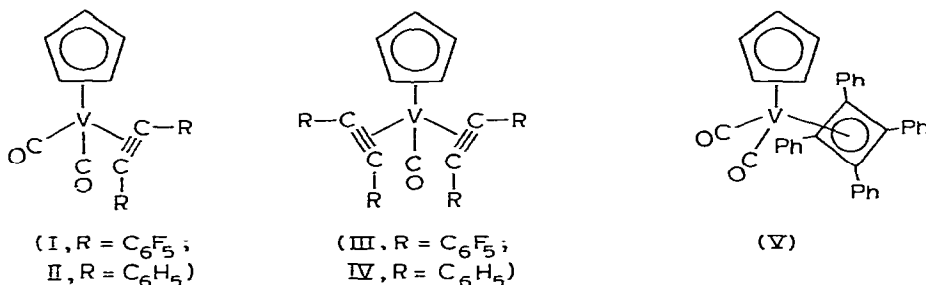
Introduction

Reactions of organometallic derivatives of vanadium and acetylenes have received relatively little attention, despite an early report by Hagihara that dicyclopentadienylvanadium caused the polymerization of various acetylenes [1]. Alkyne adducts of dicyclopentadienylvanadium have represented one course of research in this field [2–8]. The other avenue of investigation has been concerned with reactions between acetylenes and derivatives of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ [9–12]. No studies of this latter type have involved alkynes which contain electron-withdrawing substituents. We now report on photochemically and

thermally induced reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and bis(pentafluorophenyl)acetylene, $\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5$.

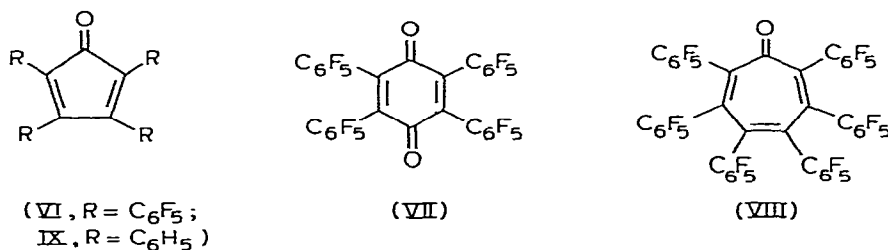
Results and discussion

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ in the presence of one equivalent of bis(pentafluorophenyl)acetylene resulted in the loss of two equivalents of carbon monoxide and formation of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$ (I) in 86% yield. Similar results were found when $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ was photolyzed with one equivalent of diphenylacetylene; $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ (II) was isolated in 75% yield. However, photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ in the presence of two equivalents of bis(pentafluorophenyl)acetylene or photolysis of I in the



presence of additional bis(pentafluorophenyl)acetylene did not yield the diacetylenic complex $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ (III), unlike similar photolyses of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ or II with diphenylacetylene, which are reported to produce $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)_2$ (IV) [10].

Bis-acetylene complex III was obtained in 75% yield, however, by the *in vacuo*, melt-phase thermolysis of I and bis(pentafluorophenyl)acetylene. In contrast, the corresponding *in vacuo* thermolysis of II and diphenylacetylene gave a cyclobutadienevanadium complex, $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\eta^4\text{-C}_4\text{Ph}_4)$ (V), in 43% yield. Thermolysis of I and bis(pentafluorophenyl)acetylene in a closed system rather than *in vacuo* resulted in the formation of a perfluorinated organic derivative, 2,3,5,6-tetrakis(pentafluorophenyl)-1,4-benzoquinone (VII), in 39% yield. A similar closed system thermolysis of II and diphenylacetylene is reported to yield V [10].



Bis-acetylene complex III could also be prepared by refluxing a mixture of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and two equivalents of bis(pentafluorophenyl)acetylene in either hexane or toluene. Also isolated from these reactions were three per-

fluorinated organic compounds, 2,3,4,5-tetrakis(pentafluorophenyl)cyclopentadienone (VI), (VII), and 2,3,4,5,6,7-hexakis(pentafluorophenyl)cycloheptatrienone (VIII). The yields of III were favored by lower reflux temperatures and shorter reflux periods (Table 1). In contrast, refluxing a toluene solution of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and two equivalents of diphenylacetylene yielded the cyclobutadienevanadium complex V (9%) and 2,3,4,5-tetraphenylcyclopentadienone (IX) (46%).

From the data in Table 1, it is apparent that III undergoes further reactions upon prolonged reflux or at higher temperatures. In order to confirm this point, a solution of III in toluene was heated at 100°C for 24 h under a carbon monoxide atmosphere. Isolated from the reaction mixture were bis(pentafluorophenyl)acetylene and $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ as well as the perfluorinated organic products VI (7%), VII (19%) and VIII (7%).

The photolysis of III in pentane solution likewise generated quinone VII in 75% yield, whereas the photolysis of IV is reported to produce cyclone IX [10]. Photolysis of III in the presence of bis(pentafluorophenyl)acetylene also resulted in formation of the fluorinated quinone derivative VII in high yield. However, photolysis of III in the presence of carbon monoxide resulted in the displacement of a coordinated acetylene ligand and addition of carbon monoxide. Isolated from this reaction were bis(pentafluorophenyl)acetylene (52%) and I (63%).

Derivatives of cyclopentadienone and *p*-benzoquinone are known to originate from reactions of acetylenes and metal carbonyl species [13–16]. However, the metal carbonyl complex usually contains a metal from the latter part of the transition metal series, and the organic moieties formed must often be cleaved from the metal by addition of acid or an oxidizing agent. Tropone derivatives have also been isolated from reactions involving metal carbonyl complexes and acetylenes [13,17,18]. Once again, the metal in the metal carbonyl derivative is from the latter part of the transition metal series, and the tropone fragment is complexed to the metal.

Nesmeyanov et al. have reported that a reaction between monoacetylene complex II and diphenylacetylene under 40 atm of CO and at 100°C for 6 h

TABLE 1

PRODUCT DISTRIBUTIONS FROM THERMAL REACTIONS OF $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ AND BIS(PENTAFLUOROPHENYL)ACETYLENE (1/2 ratio)

| Solvent | Reflux time (h) | Product yields (%) | | | |
|---------|-----------------|----------------------------------|----------------------|--------------------------------|----------------------|
| | | Diacetylene complex ^a | Quinone ^b | Cyclopentadienone ^c | Tropone ^d |
| Hexane | 12 | 36 | <3 | — | — |
| Hexane | 36 | — | 9 | — | — |
| Toluene | 4.5 | 36 | 7 | — | — |
| Toluene | 12 | 11 | 61 | 5 | 12 |

^a $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ (III). ^b 2,3,5,6-Tetrakis(pentafluorophenyl)1,4-benzoquinone (VII). ^c 2,3,5,6-Tetrakis(pentafluorophenyl)cyclopentadienone (VI). ^d 2,3,4,5,6,7-Hexakis(pentafluorophenyl)cycloheptatrienone (VIII).

produces the cyclobutadiene complex V as well as tetracyclone complex $(C_5H_5)V(CO)_2(C_4Ph_4CO)$, and have postulated a 5-membered vanadacyclopentadiene intermediate to account for these products [12]. Liebeskind et al. have likewise provided evidence for the intermediacy of metallacyclopent-3-ene-2,5-diones in the formation of quinones from alkynes and metal carbonyls [16]. While it is conceivable that various reaction pathways of these types may also be involved in the reaction between $(\eta^5-C_5H_5)V(CO)_4$ and bis(pentafluorophenyl)acetylene, pentafluorophenyl analogues of such products or intermediates were not observed in the present study. An alternative mechanism which is capable of accounting for the formation of all three fluorinated cyclopentadienone, quinone, and tropone derivatives VI–VIII from $(\eta^5-C_5H_5)V(CO)_4$ and bis(pentafluorophenyl)acetylene is outlined in Scheme 1. It should be pointed out that organometallic derivatives similar to intermediates X and XI in Scheme 1 have previously been isolated and characterized from reactions of metal carbonyl derivatives and acetylenes [19,20].

The above results demonstrate that the chemistry of the perfluorinated alkyne bis(pentafluorophenyl)acetylene does not necessarily parallel the chemistry of the non-fluorinated analogue, diphenylacetylene. This dichotomy may be due to increased carbanionic character of the coordinated fluoroacetylene [19]. Similar ionic character has been postulated for coordinated fluoro-olefin

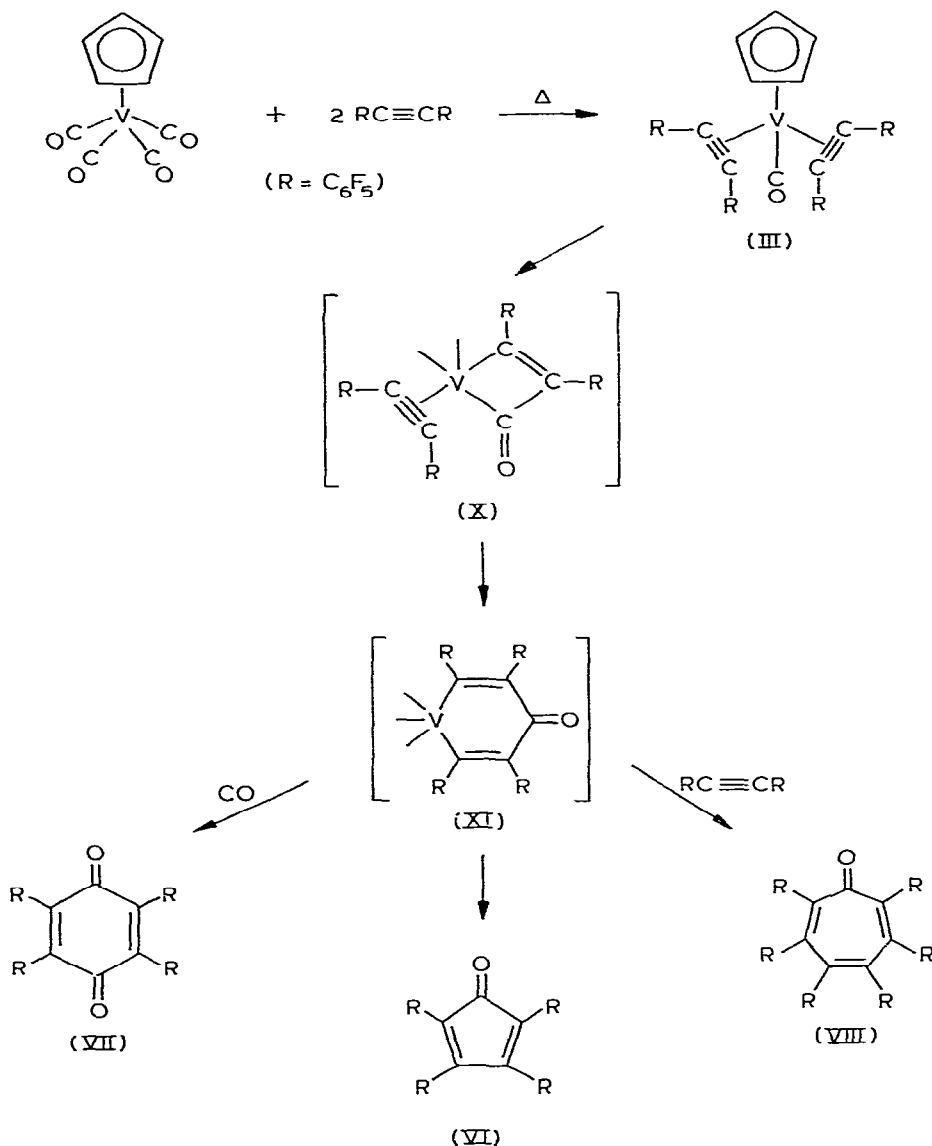


derivatives of platinum [21]. Highly electronegative fluorinated acetylenes should aid in the stabilization of such a dipolar resonance form, relative to acetylenes which do not contain electron-withdrawing substituents.

It is this carbanion-like intermediate which is thought to undergo nucleophilic attack on the carbonyl ligand, thus forming a 4-membered metallacyclic ring [19]. Metallacyclobutenone derivatives of this type have in fact been isolated from reactions between metal carbonyl species and other electron-deficient acetylenes such as hexafluoro-2-butyne [19] and dimethyl acetylenedicarboxylate [22]. From the related intermediate X (Scheme 1), the perfluorinated organic products cyclopentadienone VI, quinone VII and tropone VIII could arise. Diphenylacetylene would not stabilize the carbanionic resonance form to such an extent, and the reaction between this acetylene and $(\eta^5-C_5H_5)V(CO)_4$ could proceed via a vanadacyclopentadiene intermediate as proposed by Nesmeyanov [12].

The photolysis of I or II in the presence of triphenylphosphine resulted in the displacement of a carbon monoxide ligand and replacement by the phosphine to form $(\eta^5-C_5H_5)V(CO)(PPh_3)(RC\equiv CR)$ (XII, XIII) in yields of 69 and 58%, respectively. Complexes XII and XIII could also be isolated from the photolysis of $(\eta^5-C_5H_5)V(CO)_3(PPh_3)$ and either bis(pentafluorophenyl)acetylene or diphenylacetylene, respectively. The physical and spectral properties of XIII prepared by these photolytic reactions agree with those reported by Nesmeyanov [12] and not with those described by Hagihara [9]. However, the present results demonstrate that XIII can be isolated from the photolysis of $(\eta^5-C_5H_5)V(CO)_3-$

SCHEME 1

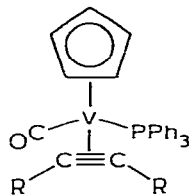


(PPh₃) and diphenylacetylene, contrary to earlier published studies [12].

Nesmeyanov has suggested that in the photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3(\text{PPh}_3)$ and diphenylacetylene, the phosphine ligand is photochemically displaced and the acetylene is coordinated to the metal to form II [11]. However, this product was never isolated, but identified only in solution. Nesmeyanov also reported that II and triphenylphosphine reacted under vacuum at 20°C to form XIII [12].

In view of these published studies, the isolation of XII and XIII from the photolyses of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3(\text{PPh}_3)$ and $\text{RC}\equiv\text{CR}$ ($\text{R} = \text{C}_6\text{F}_5, \text{C}_6\text{H}_5$) could be the result of the workup procedure, in which the solvent is removed under

reduced pressure from the photo-mixture. In effect, such a procedure could result in concentration of a mixture of photo-generated triphenylphosphine and $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{RC}\equiv\text{CR})$ (I, II), thus resulting in a secondary, non-photo-



(XII, R = C_6F_5 ;

XIII, R = C_6F_5)

chemical process involving the displacement of one coordinated carbon monoxide ligand in I or II by triphenylphosphine.

In order to test this hypothesis, a phosphine that is a gas under the photolysis conditions at 15°C , trifluorophosphine, was coordinated to vanadium. If the coordinated phosphine is liberated upon photolysis as has been shown with other phosphine-Group VB complexes [11,23–25], it would be lost from the system and could not participate in any secondary reactions. The products would therefore not contain a phosphine ligand. From the photolysis of a mixture of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3(\text{PF}_3)$ and $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{PF}_3)_2$ in the presence of diphenylacetylene, both II and IV could be isolated, thus demonstrating that the phosphine ligand was indeed photochemically displaced in this photolytic reaction.

Conclusions

The consequences of altering the alkyne from diphenylacetylene to bis(pentafluorophenyl)acetylene are profound when these acetylenes interact with $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$. Both thermally- and photochemically-induced reactions are affected. Rather than forming products consistent with a vanadacyclopentadiene intermediate, as is the case with diphenylacetylene, the products obtained from reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and bis(pentafluorophenyl)acetylene appear to be derived from a vanadacyclohexadienone intermediate. Photochemical reactions between either acetylene and $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ lead to mono-acetylene products of the type $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{RC}\equiv\text{CR})$, whereas these products are not observed in thermal reactions. In vacuo, melt-phase thermal reactions between the mono-acetylene complexes and a second equivalent of acetylene lead to a cyclobutadiene derivative $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\eta^4\text{-C}_4\text{Ph}_4)$ in the case of diphenylacetylene, and to a diacetylenic complex $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})\text{-}(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ in the case of bis(pentafluorophenyl)acetylene. On the other hand, $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$ under photolytic conditions is resistant to further substitution by bis(pentafluorophenyl)acetylene, while a similar photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ and diphenylacetylene leads to the diacetylenic complex $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)_2$. In contrast to $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)_2$, thermolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ produces quinone and cycloheptatrienone as well as cyclopentadienone deriva-

tives. It is evident that the nature of the acetylene therefore exerts considerable control over the type of reactions that are mediated by $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$.

Experimental

All manipulations of air-sensitive compounds were carried out under a purified argon atmosphere using Schlenk techniques. The argon was dried with H_2SO_4 and P_2O_5 , and trace oxygen was removed using BTS catalyst. Pentane, hexane, benzene and toluene were dried over calcium hydride and freshly distilled under argon. Diethyl ether and THF were predried over sodium and then distilled under argon from sodium/benzophenone. Column chromatography was performed under argon using Alfa-Ventron neutral alumina. The alumina was predried in a 60°C oven overnight and then heated with mixing under vacuum for 1 h and deactivated with deaerated, distilled water (5% by weight). Melting points were performed under argon and are corrected. Photolyses were conducted with a 450 W Hanovia photochemical lamp located in a water-cooled immersion well. This unit was placed 1–2 cm from a water-jacketed Schlenk tube containing the solution to be photolyzed. $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ [26], $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3(\text{PPh}_3)$ [9], $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3(\text{PF}_3)$ and $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{PF}_3)_2$ [27], diphenylacetylene [28], and bis(pentafluorophenyl)acetylene [29] were prepared by literature methods. Triphenylphosphine was purchased from Alfa Products, Ventron Division of Thiokol Corporation. ^1H NMR spectra were recorded on a Varian A-60 spectrometer. IR spectra were taken on a Perkin–Elmer 237B or on a Beckman IR-10 spectrometer. Ultraviolet-visible spectra were recorded on a Perkin–Elmer 202 ultraviolet-visible spectrometer. Mass spectra were obtained on a Perkin–Elmer–Hitachi RMU-6L instrument at 70 eV by Mr. E. Guzik. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, MA.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ in the presence of bis(pentafluorophenyl)acetylene (1/1 ratio)

A solution of 1.20 g (5.26 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and 1.90 g (5.31 mmol) of bis(pentafluorophenyl)acetylene in 200 ml of pentane was photolyzed in a water-jacketed Schlenk tube for 3 h. Upon irradiation, the orange solution immediately turned to green and gas was evolved. Next, the solvent was removed by vacuum and the green residue chromatographed on alumina. Hexane eluted a small yellow band. A large green band was eluted with a 5/1 mixture of hexane/benzene. This band was collected and the solvent removed by vacuum, leaving 2.40 g (86%) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$. The air-sensitive green solid was recrystallized from hexane, m.p. $90\text{--}92^\circ\text{C}$. (Found: C, 47.76; H, 0.89. $\text{C}_{21}\text{H}_5\text{F}_{10}\text{O}_2\text{V}$ calcd.: C, 47.57; H, 0.95%). Mass spectrometry: m/e 530 (M^+), 502 ($M - \text{CO}^+$), 474 ($M - 2 \text{CO}^+$), 358 ($\text{C}_{14}\text{F}_{10}^+$), 289 ($\text{C}_{12}\text{F}_7^+$), 179 (C_7F_5^+), 116 ($\text{C}_5\text{H}_5\text{V}^+$), 51 (V^+). NMR (C_6D_6): τ 4.98 (s, C_5H_5); (acetone- d_6): τ 4.17 (s, C_5H_5); (CS_2): τ 4.38 (s, C_5H_5). IR (Nujol): $\nu(\text{CO})$ 2025, 1960 cm^{-1} ; $\nu(\text{C}\equiv\text{C})$ 1700–1650 cm^{-1} .

Photolysis of (η^5 -C₅H₅)V(CO)₄ in the presence of bis(pentafluorophenyl)acetylene (1/2 ratio)

Photolysis of a 250-ml pentane solution of 0.60 g (2.63 mmol) of (η^5 -C₅H₅)V(CO)₄ and 1.88 g (5.25 mmol) of bis(pentafluorophenyl)acetylene in a water-jacketed Schlenk tube was performed for 12 h. The orange solution turned green. The solvent was removed by vacuum and the green residue chromatographed on alumina. Bis(pentafluorophenyl)acetylene and (η^5 -C₅H₅)V(CO)₂(C₆F₅C≡CC₆F₅) were isolated. Only traces (<10 mg) of (η^5 -C₅H₅)V(CO)(C₆F₅C≡CC₆F₅)₂ were obtained.

Thermal reaction of (η^5 -C₅H₅)V(CO)₄ and bis(pentafluorophenyl)acetylene (1/2 ratio)

A solution of 0.62 g (2.72 mmol) of (η^5 -C₅H₅)V(CO)₄ and 1.94 g (5.42 mmol) of bis(pentafluorophenyl)acetylene in 125 ml of toluene was refluxed for 12 h. Gas was evolved, and the solution changed from orange to green. The solvent was removed by vacuum, and the green residue was chromatographed on alumina. A bright yellow band was eluted with 10/1 hexane/benzene. The band was collected, and the solvent was removed under reduced pressure, leaving 0.24 g (11%) of bright yellow, air-stable (η^5 -C₅H₅)V(CO)(C₆F₅C≡CC₆F₅)₂. Recrystallization from 10/1 pentane/toluene at -20°C resulted in formation of large orange crystals, m.p. 151°C. (Found: C, 47.39; H, 0.73; F, 44.11. C₃₄H₅F₂₀O₂ calcd.: C, 47.47; H, 0.59; F, 44.17%). Mass spectrometry: *m/e* 860 (*M*⁺), 832 (*M* - CO⁺), 744 (*M* - C₅H₅V⁺), 716 (*M* - C₅H₅V, CO⁺), 358 (C₁₄F₁₀⁺), 116 (C₅H₅V⁺). NMR (C₆D₆): τ 4.97 (s, C₅H₅); (acetone-*d*₆): τ 4.22 (s, C₅H₅). IR (KBr): ν (CO) 2025 cm⁻¹; ν (C≡C) 1790, 1760 cm⁻¹.

Elution with benzene/ethyl ether (1/1) produced a wide, pale-orange band. The band was collected and the air-stable solution taken to dryness under vacuum. Recrystallization from a 1/1 mixture of toluene/pentane gave 1.28 g (61%) of pale yellow 2,3,5,6-tetrakis(pentafluorophenyl)-1,4-benzoquinone. This organic derivative may also be sublimed at 120°C and 10⁻³ Torr, m.p. 177–178°C. (Found: C, 46.71; H, <0.1, F, 48.8. C₃₀F₂₀O₂ calcd.: C, 46.66; H, 0.00; F, 49.20%). Mass spectrometry: *m/e* 772 (*M*⁺), 744 (*M* - CO⁺), 728 (*M* - CO, O⁺), 716 (*M* - 2 CO⁺), 358 (C₁₄F₁₀⁺), 195 (C₇F₅O⁺). IR (KBr): ν (CO) 1743 cm⁻¹; ν (C=C) 1651 cm⁻¹. UV/Visible (methanol): 402 nm, ϵ 1.62 × 10² cm⁻¹ l⁻¹ mol; 331 nm, ϵ = 1.62 × 10³; 266 nm, ϵ = 1.62 × 10⁴.

Tetrahydrofuran eluted a small dark green band, while acetone eluted a bright orange band. The latter air-stable band was collected and the solvent removed by evaporation, leaving 0.10 g (5%) of red-orange 2,3,4,5-tetrakis(pentafluorophenyl)cyclopentadienone, m.p. 232–235°C (lit. m.p. 232–233°C) [30]. Mass spectrometry: *m/e* 744 (*M*⁺), 728 (*M* - O⁺), 716 (*M* - CO⁺), 358 (C₁₄F₁₀⁺), 339 (C₁₄F₉⁺). IR (KBr): ν (CO) 1730 cm⁻¹; ν (C=C) 1640 cm⁻¹.

Methanol eluted a yellow band. Collection of this air-stable band and removal of the solvent by evaporation gave 0.24 g (12%) of light-sensitive, yellow 2,3,4,5,6,7-hexakis(pentafluorophenyl)cycloheptatrienone. Mass spectrometry: *m/e* 1102 (*M*⁺), 1090 (*M* - C⁺), 1086 (*M* - O⁺), 1083 (*M* - F⁺), 1074 (*M* - CO⁺), 1055 (*M* - CO, F⁺), 744 (C₂₉F₂₀O⁺), 716 (C₂₈F₂₀⁺), 358 (C₁₄F₁₀⁺), 195 (C₇F₅O⁺). IR (KBr): ν (CO) 1685 cm⁻¹.

When 0.63 g (2.76 mmol) of (η^5 -C₅H₅)V(CO)₄ and 1.95 g (5.45 mmol) of

bis(pentafluorophenyl)acetylene were refluxed in 50 ml of toluene for 4.5 h and the reaction mixture worked up by chromatography on alumina, only two products were obtained: $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ (0.85 g, 36%) and 2,3,5,6-tetrakis(pentafluorophenyl)-1,4-benzoquinone (0.16 g, 7%).

In a similar reaction, 0.36 g (1.58 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and 1.09 g (3.04 mmol) of bis(pentafluorophenyl)acetylene were refluxed for 12 h in hexane. Workup via column chromatography on alumina gave 0.49 g (36%) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ and a trace (<3%) of the quinone derivative.

Prolonged hexane reflux (36 h) of 1.05 g (4.61 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and 3.29 g (9.19 mmol) of bis(pentafluorophenyl)acetylene gave no $(\eta^5\text{-C}_5\text{H}_5)\text{-V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ after column chromatography. The quinone derivative was isolated in 9% yield following chromatography.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ in the presence of diphenylacetylene (1/1 ratio)

A solution of 0.83 g (3.64 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and 0.65 g (3.65 mmol) of diphenylacetylene in 200 ml of pentane was photolyzed in a water-jacketed Schlenk tube. Upon irradiation, the orange solution evolved gas and the color turned to green. Following 3 h of photolysis, the solvent was removed by vacuum and the green residue was chromatographed on alumina. A small yellow band was eluted with hexane. A green band was eluted with a 5/1 hexane/benzene mixture. This band was collected and the solvent removed by vacuum, leaving 0.96 g (75%) of green, air-sensitive $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2\text{-}(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ [10]. NMR (acetone- d_6): τ 4.27 (s, 5 H, C_5H_5), 2.48 (m, 10 H, C_6H_5); (CS_2): τ 4.50 (s, 5 H, C_5H_5), 2.63 (m, 10 H, C_6H_5). IR (Nujol): $\nu(\text{CO})$ 1980, 1915 cm^{-1} ; $\nu(\text{C}\equiv\text{C})$ 1700 cm^{-1} .

Thermal reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and diphenylacetylene (1/2 ratio)

An orange solution of 1.00 g (4.39 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and 1.60 g (8.99 mmol) of diphenylacetylene in 75 ml of toluene was refluxed for 17 h. Gas was evolved and the color of the solution turned to yellow-brown. The mixture was cooled and the solvent removed by vacuum. The resulting residue was chromatographed on alumina. Pentane elution removed traces of unreacted starting materials. A 2/1 pentane/benzene mixture eluted an orange band. Removal of the solvent from this band by vacuum produced 0.20 g (9%) of air-stable, orange $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\eta^4\text{-C}_6\text{Ph}_4)$ [10]. Mass spectrometry: m/e 528 (M^+), 472 ($M - 2\text{CO}^+$), 384 ($M - \text{C}_5\text{H}_5\text{V}, \text{CO}^+$), 368 ($\text{C}_{29}\text{H}_{20}^+$), 253 ($\text{C}_{20}\text{H}_{13}^+$), 178 ($\text{C}_{20}\text{H}_{13}^+$), 178 ($\text{C}_{14}\text{H}_{10}^+$), 116 ($\text{C}_5\text{H}_5\text{V}^+$). NMR (CS_2): τ 5.23 (s, 5 H, C_5H_5), 2.92 (m, 20 H, C_6H_5). IR (toluene): $\nu(\text{CO})$ 1980, 1925 cm^{-1} .

The column was then eluted with diethyl ether, producing an intensely purple band. This air-stable band was collected, and the solvent was removed by evaporation, leaving 0.80 g (46%) of 2,3,4,5-tetraphenylcyclopentadienone, m.p. 213–215°C (lit. m.p. 217–218°C) [31]. NMR (acetone- d_6): τ 2.71 (s, C_6H_5). IR (KBr): $\nu(\text{CO})$ 1710 cm^{-1} .

A mixture of 0.75 g (3.23 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and 1.18 g (6.63 mmol) of diphenylacetylene was refluxed for 18 h in 75 ml of hexane. Only starting materials and no products were isolated by column chromatography of the reaction mixture.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$ (I) in the presence of bis(pentafluorophenyl)acetylene

$(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$ (1.03 g, 1.94 mmol) and bis(pentafluorophenyl)acetylene (0.69 g, 1.93 mmol) were dissolved in 50 ml of pentane and photolyzed in a water-jacketed Schlenk tube for 5 h. No color change or gas evolution was observed. The solvent was removed by vacuum and the green residue chromatographed on alumina. Hexane eluted unreacted bis(pentafluorophenyl)acetylene. A mixture of 10/1 hexane/benzene eluted a green band. Removal of the solvent under reduced pressure gave green $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$.

Thermolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$ (I) and bis(pentafluorophenyl)acetylene in vacuo

A mixture of 0.74 g (1.4 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$ and 0.52 g (1.5 mmol) of bis(pentafluorophenyl)acetylene was placed in a Schlenk tube, and the tube was evacuated. The green solid mixture was placed in a 100°C mineral oil bath. The mixture was melted and gas was evolved. The generated gas was periodically removed by re-evacuation of the system. The green melt turned to a yellow melt, then to a yellow solid. Following 30 min of heating, the mixture was cooled and chromatographed on alumina. Pentane eluted unreacted bis(pentafluorophenyl)acetylene, while 1/1 pentane/benzene eluted a yellow-orange band. Removal of the solvent from this band by vacuum produced 0.90 g (75%) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$.

Thermolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$ (I) and bis(pentafluorophenyl)acetylene in a closed system

$(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$ (0.54 g, 1.0 mmol) and bis(pentafluorophenyl)acetylene (0.73 g, 2.0 mmol) were mixed in a pressure Schlenk tube and heated to 100–120°C in a mineral oil bath, causing the mixture to melt. During the 3 h heating, the melt changed from a green color to black. The mixture was cooled and chromatographed on alumina. Elution with benzene brought down a yellow-orange band. This air-stable band was collected and the solvent removed by evaporation, leaving 0.28 g (39%) of 2,3,5,6-tetrakis(pentafluorophenyl)-1,4-benzoquinone.

Thermolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ (II) and diphenylacetylene in vacuo

$(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ (0.80 g, 2.2 mmol) and diphenylacetylene (0.41 g, 2.3 mmol) were mixed in a Schlenk tube, and the system was evacuated. The solid green mixture was placed in a 105–110°C mineral oil bath. The mixture melted and some gas was evolved. The system was periodically re-evacuated. The green melt turned to a yellow-brown melt, then to a yellow-brown solid. Following 30 min of heating, the mixture was cooled and chromatographed on alumina. Pentane eluted unreacted diphenylacetylene. A 5/1 mixture of pentane/benzene eluted a small green band. Removal of the solvent by vacuum gave 25 mg (3%) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$. Elution with 1/5 pentane/benzene produced a yellow-orange band. Collection of this band followed by removal of the solvent under reduced pressure yielded 0.51 g (43%) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\eta^4\text{-C}_4\text{Ph}_4)$.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ (III)

A mixture of 0.28 g (0.33 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ in 35 ml of pentane was irradiated in a water-jacketed Schlenk tube for 12 h. The color of the solution changed from yellow-orange to dark green to blue. The solvent was removed by vacuum and the residue chromatographed on alumina. Two yellow bands were eluted, one with 1/1 pentane/benzene, the other with benzene. Removal of the solvent from the first band yielded 70 mg (25%) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$. Removal of the solvent from the second band gave 95 mg (75% based on CO) of pale yellow 2,3,5,6-tetrakis(pentafluorophenyl)-1,4-benzoquinone.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ (III) in the presence of carbon monoxide

A solution of 0.70 g (0.81 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ in 50 ml of pentane in a pressure Schlenk tube was frozen in liquid nitrogen and the system was evacuated. Approximately 100 ml of gaseous carbon monoxide was condensed into the system. The closed Schlenk tube was warmed and photolyzed for 20 h in a 15°C water bath. The yellow solution turned green. The solvent was removed by vacuum and the residue chromatographed on alumina. The pentane forerun was collected and the solvent evaporated, leaving 0.15 g (52%) of bis(pentafluorophenyl)acetylene. Further elution with pentane produced a green band which was collected. The solvent was removed from this band by vacuum, leaving 0.27 g (63%) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$. Benzene elution produced a yellow band which when taken to dryness by vacuum yielded 20 mg (3%) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ (III) in the presence of bis(pentafluorophenyl)acetylene

$(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ (0.30 g, 0.35 mmol) and bis(pentafluorophenyl)acetylene (0.13 g, 0.36 mmol) were dissolved in 50 ml of pentane and photolyzed for 19 h in a water-jacketed Schlenk tube. The solution changed from yellow-orange to green to blue. The solvent was removed by vacuum and the residue was chromatographed on alumina. A mixture of 1/1 pentane/benzene eluted a yellow-orange band. This band was collected and the solvent removed by vacuum, leaving 25 mg (8%) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$. Benzene eluted a wide yellow band. Removal of the solvent from this band by vacuum left 0.115 g (85% based on CO) of 2,3,5,6-tetrakis(pentafluorophenyl)-1,4-benzoquinone.

Thermolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ (III) in the presence of carbon monoxide

A yellow solution of 0.47 g (0.55 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)_2$ in 30 ml of toluene contained in a pressure Schlenk tube was frozen in liquid nitrogen and then evacuated. Approximately 150 ml of gaseous carbon monoxide was condensed into the frozen system. The sealed reaction mixture was then warmed to room temperature and placed in a 100°C mineral oil bath. The mixture was heated for 24 h during which time the yellow solution became dark green. The solution was cooled, and the solvent was removed by vacuum.

The residue was chromatographed on alumina. Pentane elution produced a mixture of bis(pentafluorophenyl)acetylene and $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$. A 1/1 mixture of pentane/benzene eluted a wide yellow band. This air-stable band was collected and taken to dryness by evaporation, yielding 80 mg (19%) of 2,3,5,6-tetrakis(pentafluorophenyl)-1,4-benzoquinone. Elution with acetone brought an orange band down the column. The solvent was removed from this air-stable band by evaporation, giving 30 mg (7%) of 2,3,4,5-tetrakis(pentafluorophenyl)-cyclopentadienone. The column support was then dried under vacuum and extracted with 3×50 ml of acetone. The bright yellow solution was collected and the solvent removed by evaporation, leaving 30 mg (7%) of 2,3,4,5,6,7-hexakis(pentafluorophenyl)cycloheptatrienone.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ in the presence of bis(pentafluorophenyl)acetylene

A solution of 0.70 g (1.51 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ and 0.54 g (1.51 mmol) of bis(pentafluorophenyl)acetylene in 250 ml of benzene was photolyzed in a water-jacketed Schlenk tube for 6 h. The orange solution evolved gas and turned dark red upon irradiation. The solvent was then removed by vacuum. The red residue was chromatographed on alumina. A small yellow band was eluted with hexane. A 5/1 hexane/benzene mixture eluted an orange-red band. The band was collected and the solvent removed under reduced pressure, yielding 0.75 g (65%) of relatively air-stable, yellow-orange $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3](\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$. It was recrystallized from hexane, m.p. 112–114°C. (Found: C, 58.97; H, 2.72; P, 4.20. $\text{C}_{38}\text{H}_{20}\text{F}_{10}\text{OPV}$ calcd.: C, 59.21; H, 2.64; P, 4.05%). Mass spectrometry: m/e 764 (M^+), 736 ($M - \text{CO}^+$), 358 ($\text{C}_{14}\text{F}_{10}^+$), 262 ($\text{C}_{18}\text{H}_{15}\text{P}^+$), 183 ($\text{C}_{12}\text{H}_8\text{P}^+$), 116 ($\text{C}_5\text{H}_5\text{V}^+$), 108 ($\text{C}_6\text{H}_5\text{P}^+$). NMR (acetone- d_6): τ 4.71 (d, 5 H, $J(\text{H}-\text{P})$ 2.5 Hz, C_5H_5), 2.90 (m, 15 H, C_6H_5); (CS_2); τ 4.90 (d, 5 H, $J(\text{H}-\text{P})$ 2 Hz, C_5H_5), 2.67 (m, 15 H, C_6H_5). IR (KBr): $\nu(\text{CO})$ 1905 cm^{-1} ; $\nu(\text{C}\equiv\text{C})$ 1635 cm^{-1} .

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ in the presence of diphenylacetylene

Photolysis of a solution of 0.48 g (1.0 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ and 0.18 g (1.0 mmol) of diphenylacetylene in 200 ml of benzene in a water-jacketed Schlenk tube resulted in rapid gas evolution and color changes from orange to olive green to dark yellow. Following 4 h of irradiation, the solvent was removed from the reaction mixture by vacuum. The residue was chromatographed on alumina. The only band eluted was brought down the column with 5/1 hexane/benzene. The band was collected and the solvent removed under reduced pressure, leaving 0.28 g (36%) of golden-orange, air-stable $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3](\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$, m.p. 109–110°C dec. (lit. m.p. 110–112°C dec.) [12]. (Found: C, 78.35; H, 5.43; P, 5.08. $\text{C}_{38}\text{H}_{30}\text{OPV}$ calcd.: C, 78.08; H, 5.17; P, 5.30%). Mass spectrometry: m/e 584 (M^+), 556 ($M - \text{CO}^+$), 262 ($\text{C}_{18}\text{H}_{15}\text{P}^+$), 183 ($\text{C}_{12}\text{H}_8\text{P}^+$), 178 ($\text{C}_{14}\text{H}_{10}^+$), 116 ($\text{C}_5\text{H}_5\text{V}^+$), 108 ($\text{C}_6\text{H}_5\text{P}^+$). NMR (CS_2): τ 5.00 (d, 5 H, $J(\text{H}-\text{P})$ 2 Hz, C_5H_5), 2.80 (m, 25 H, C_6H_5). IR (Nujol): $\nu(\text{CO})$ 1860 cm^{-1} ; $\nu(\text{C}\equiv\text{C})$ 1645 cm^{-1} .

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3\text{PF}_3$ and $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{PF}_3)_2$ in the presence of diphenylacetylene

A solution containing 0.59 g of a mixture of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3\text{PF}_3$ and

$(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{PF}_3)_2$ together with 1.00 g (5.62 mmol) of diphenylacetylene in 250 ml of pentane in a water-jacketed Schlenk tube was photolyzed for 7.5 h. The solution turned green, and gas was evolved. The solvent was removed under reduced pressure and the residue chromatographed on alumina. A 10/1 pentane/benzene mixture eluted a green band. Removal of the solvent by vacuum gave 0.44 g of green $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$. A 1/1 pentane/benzene mixture eluted a yellow band. Collection of this band followed by removal of the solvent under reduced pressure gave 0.10 g of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)_2$ [10]. NMR (CS_2): τ 4.72 (s, 5H, C_5H_5), 2.88 (m, 20 H, C_6H_5). IR (KBr): $\nu(\text{CO})$ 1965 cm^{-1} ; $\nu(\text{C}\equiv\text{C})$ 1815 cm^{-1} .

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$ (I) in the presence of triphenylphosphine

A 2 h irradiation of 0.67 g (1.26 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$ and 0.33 g (1.26 mmol) of triphenylphosphine in 200 ml of pentane resulted in the evolution of gas and a color change from green to red-brown. The solvent was removed from the reaction mixture by vacuum and the residue chromatographed on alumina. Hexane eluted a small yellow band. Removal of the solvent from this band by vacuum yielded 0.66 g (69%) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})\text{[P}(\text{C}_6\text{H}_5)_3\text{]}(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ (II) in the presence of triphenylphosphine

$(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ (0.77 g, 2.2 mmol) and triphenylphosphine (0.58 g, 2.2 mmol) were dissolved in 250 ml of pentane in a water-jacketed Schlenk tube and photolyzed for 2 h. The color of the solution changed from green to yellow. A yellow precipitate also formed, and gas was evolved. The solvent was removed from the reaction mixture by vacuum and the resulting solid chromatographed on alumina. Hexane eluted a small green band. A 2/1 mixture of hexane/benzene brought a golden orange band down the column. This band was collected and the solvent removed under reduced pressure to yield 0.75 g (58%) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})\text{[P}(\text{C}_6\text{H}_5)_3\text{]}(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ [12].

Thermolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})\text{[P}(\text{C}_6\text{H}_5)_3\text{]}(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$ (XII) and bis(pentafluorophenyl)acetylene in a closed system

A mixture of 0.38 g (0.50 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})\text{[P}(\text{C}_6\text{H}_5)_3\text{]}(\text{C}_6\text{F}_5\text{C}\equiv\text{CC}_6\text{F}_5)$ and 0.18 g (0.50 mmol) of bis(pentafluorophenyl)acetylene was heated in a sealed pressure Schlenk tube for 2 h in a 95–100°C mineral oil bath. The orange mixture melted and turned purple. Alumina chromatography yielded 2,3,5,6-tetrakis(pentafluorophenyl)-1,4-benzoquinone upon elution with benzene.

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