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The Crystal and Molecular Structure of *trans*-Chloro-2-(phenylazo)phenylbis(triethylphosphine)palladium(II)

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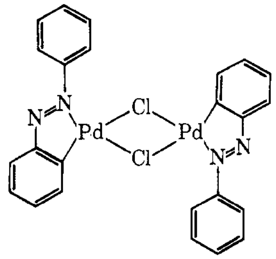
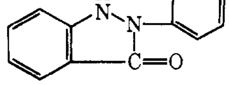
The structure of the compound *trans*-chloro-2-(phenylazo)phenylbis(triethylphosphine)palladium(II), $PdCl(C_{12}H_9N_2)(P(C_2H_5)_3)_2$, has been determined by single-crystal X-ray diffractometry. This complex crystallizes in the space group $P2_1/c$ (C_{2h}^5) with eight molecules in a unit cell of dimensions $a = 19.521$ (7) Å, $b = 16.694$ (6) Å, $c = 17.445$ (5) Å, and $\beta = 105.70$ (3)°. The structure was refined by least-squares methods to a conventional R factor of 9.0% for the 2862 observed reflections. The palladium atom is surrounded in an approximately planar fashion by two *trans* phosphorus atoms, a chlorine atom, and a σ-bonded carbon atom of the 2-(phenylazo)phenyl group. The average Pd–Cl distance of 2.382 (5) Å *trans* to the σ-bonded carbon atom is long and the Pd–C distance of 1.994 (15) Å is normal. Bond distances and angles within the 2-(phenylazo)phenyl ligand do not differ significantly from those in *trans*-azobenzene. $PdCl(C_{12}H_9N_2)(P(C_2H_5)_3)_2$ is formed in the reaction of the dimer $[PdCl(C_{12}H_9N_2)]_2$ with 4 equiv of phosphine and is a member of a new class of compounds containing the σ-bonded 2-(phenylazo)phenyl group.

Introduction

Transition metals undergo a variety of reactions with azobenzene. When $Fe(CO)_5$ is irradiated in the presence of azobenzene,[1] an *o*-semidine derivative is formed in which the N=N linkage has been broken. An *o*-semidine derivative[2] is also obtained in the reaction of dicyclopentadienylcobalt or dicyclopentadienylcobalt dicarbonyl with azobenzene. However, if the N=N bond is retained in the reaction with azobenzene, the 2-(phenylazo)phenyl group can function either as a bidentate or a monodentate ligand. Examples of the former behavior include the chloro-2-(phenylazo)phenylpalladium dimer[3] (I), tricarbonyl-2-(phenylazo)phenylcobalt, and tetracarbonyl-2-(phenylazo)phenylmanganese[4] where presumably the *ortho* carbon atom and the nitrogen atom farthest from the *ortho* position bond to the metal. By contrast, reaction of complex I with carbon monoxide[5] and the $Co_2(CO)_8$-catalyzed carbonylation[6] of azobenzene both form 2-phenyl-1H-indazolone (II). In each of these reactions a σ-bonded intermediate is thought to be involved in which the 2-(phenylazo)phenyl moiety acts as a monodentate ligand.



I



II

When dimer I is treated with 4 equiv of triethylphosphine, a complex of the stoichiometry $PdCl(C_{12}H_9N_2)(P(C_2H_5)_3)_2$ (III) is formed. Since none of the complexes of azobenzene in which the N=N bond is retained has been investigated by X-ray methods, it was of interest to establish the coordination geometry of III by a crystal structure determination. An earlier communication[7] describes the preliminary results of this work.

Collection and Reduction of Data

A sample of $PdCl(C_{12}H_9N_2)(P(C_2H_5)_3)_2$ was kindly supplied by Professor R. W. Siekman. Orange crystals, suitable for X-ray studies, were obtained from slow evaporation of methylene chloride–hexane solutions. Examination of the crystals by Weissenberg and precession photographs showed the following absences indicative of the space group $P2_1/c$ (no. 14, C_{2h}^5): $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$. Unit cell dimensions were determined by least-squares refinement of 16 reflections, $25 \leq 2\theta \leq 75°$, centered on a GE XRD-5 diffractometer using Cu K$\bar{\alpha}$ radiation (λ 1.5418 Å) and a takeoff angle of 2°. The results are $a = 19.521$ (7) Å, $b = 16.694$ (6) Å, $c = 17.445$ (5) Å, and $\beta = 105.70$ (3)°. For eight molecules in the unit cell, the calculated density is 1.39 g/cm^3. A density range of 1.25–1.40 g/cm^3 was found by flotation in phosphoric acid solutions. (The complex is very soluble in all common solvents in this density range.)

For intensity measurements, a crystal of dimensions $0.07 \times 0.2 \times 0.1$ mm along a, b, and c, respectively, was mounted on a GE XRD-5 automated diffractometer with its b axis parallel to the φ axis. A kinematic intensity profile[8] for several reflections showed a width at half-maximum intensity of approximately 0.45° using the ω-scan technique and a takeoff angle of 4°.

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[1] M. M. Bagga, W. T. Flannigan, G. R. Knox, and P. L. Pauson, *J. Chem. Soc. C*, 1534 (1969).

[2] T. Joh, N. Hagihara, and S. Murahashi, *Bull. Chem. Soc. Jap.*, **40**, 661 (1967).

[3] A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, **87**, 3272 (1965).

[4] R. F. Heck, *ibid.*, **90**, 313 (1968).

[5] A. C. Cope, Abstracts, 19th National Organic Symposium, Tempe, Ariz., June 13–17, 1965, p 42.

[6] S. Horiie and S. Murahashi, *Bull. Chem. Soc. Jap.*, **33**, 88 (1960).

[7] R. W. Siekman and D. L. Weaver, *Chem. Commun.*, 1021 (1968).

[8] L. E. Alexander and G. S. Smith, *Acta Crystallogr.*, **15**, 983 (1962).

Intensities were collected at room temperature by the θ–2θ scan technique using Mo Kα radiation filtered through 2 mils of Nb foil. The width of the pulse height analyzer was set to accept 90% of the radiation centered on the Mo Kα peak. A symmetric scan range of 2°, $2 < 2\theta < 20°$, and 3°, $20 \leq 2\theta \leq 42°$, at a scan rate of 2°/min was used. Lower and upper stationary background counts of 20 sec each were recorded. The quality and alignment of the crystal were monitored throughout data collection by three standards: two at $\chi = 0°$ and one at $\chi = 90°$. A slow decrease of 15% of the total intensity occurred during data collection. All reflections were put on a common scale and corrected for the intensity decrease by use of the three standards. Twelve reflections exceeded the range of linearity of the counter and were measured using a 5-mil thickness of Nb foil.

A total of 6314 independent reflections up to $2\theta_{\text{Mo K}\alpha} \leq 42°$ ($(\sin\theta)/\lambda \leq 0.51$) were measured. These intensities were corrected for background, Lorentz, and polarization factors and reduced to values of F^2. Standard deviations from counting statistics were assigned each reflection according to the formula $\sigma(I) = [CT + 0.25(t_c/t_B)^2(B_1 + B_2) + (PI)^2]^{1/2}$, where CT is the total integrated count in time t_c, t_B is the time required for each background count B_1 and B_2, and P is a factor introduced to correct for fluctuations encountered during data collection. A value of 0.045 was chosen for P. Of the 6314 intensities measured, a total of 2862 independent reflections were classified as observed using the criterion $I > 2.0\sigma(I)$. These observed reflections were used in the solution and refinement of the structure. The linear absorption coefficient for Mo Kα radiation is 9.17 cm^{-1} and no absorption corrections were applied to the data. Transmission coefficients range from about 0.91 to 0.94 for all of the data.

Solution and Refinement of the Structure

Throughout full-matrix least-squares refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weight w is $1/\sigma^2(F_o)$ and $\sigma(F_o)$, the standard deviation of F_o, is equal to $\sigma(F_o^2)/2F_o$. The usual discrepancy factors were defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

The two palladium atoms were readily located from a three-dimensional Patterson function calculated using the 2862 independent observed reflections. From a Fourier synthesis phased on these two atoms, the six phosphorus and chlorine atom positions were found. Two cycles of least-squares refinement based on the contribution to the structure factors from these eight atoms gave a value of R_1 of 29.0%. Further electron and difference electron density maps located the remaining 52 carbon and nitrogen atoms. When positional and isotropic thermal parameters were varied for all 60 atoms, an R_1 of 10.5% and an R_2 of 10.7% resulted. Anisotropic temperature factors were assigned to the two Pd, four P, and two Cl atoms. Further full-matrix refinement varying all 281 parameters lowered the values of the residuals, R_1 to 9.0% and R_2 to 8.9%.

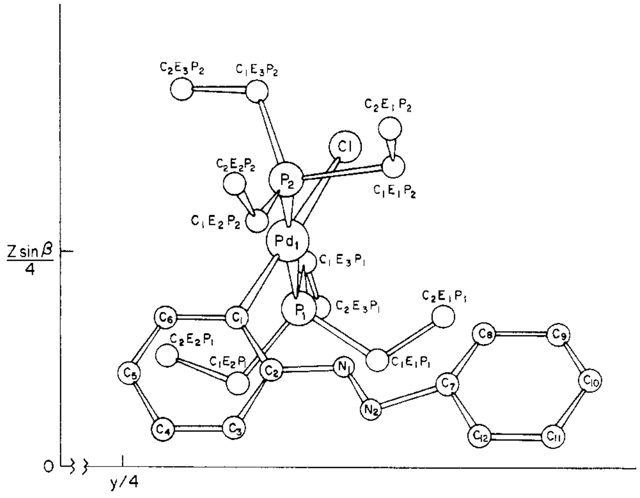

Figure 1.—A molecule of $PdCl(Azb)(P(C_2H_5)_3)_2$ viewed along a.

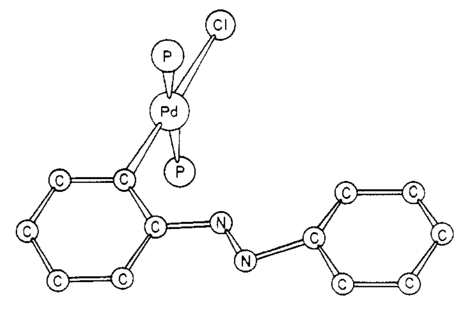

Figure 2.—The inner coordination sphere in $PdCl(Azb)(P(C_2H_5)_3)_2$ projected down the a axis. The 2-(phenylazo)phenyl group is included.

During the later stages of refinement, it was noted that seven carbon atoms (C(1)*E(1)P(2)*, C(2)*E(1)P(2)*, C(2)*E(2)P(2)*, C(1)*E(1)P(4)*, C(2)*E(1)P(4)*, C(1)*E(2)P(4)*, and C(2)*E(2)P(4)*) of the triethylphosphine ligands had unreasonably high thermal parameters and coordinates which gave carbon–carbon distances not in agreement with expectation. A difference Fourier map was phased on structure factors which excluded contributions from these seven atoms. Diffuse areas of electron density (1.5–0.75 e$^-$/Å^3) were observed in the locations where these atoms had been previously positioned. This electron density may be compared with an average value obtained from an observed Fourier synthesis of approximately 4.5 e$^-$/Å^3 ($B \approx 5.0$ Å^2) for the carbon atoms of the two 2-(phenylazo)phenyl groups. An attempt was made to resolve this disorder by assigning the carbon atoms fractional positions, fractional weights, and isotropic thermal parameters of $B = 12.0$ Å^2 in accordance with the difference electron density map. Least-squares refinement of all parameters but those for the seven carbon atoms converged to $R_1 = 9.3\%$ and $R_2 = 9.5\%$. A Hamilton R factor ratio test[9] shows that the ordered model ($R_2 = 8.9\%$) is an improvement over the disordered model ($R_2 = 9.5\%$) which is significant at a level of confidence

[9] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) (IN ELECTRONS) FOR $PdCl(C_{12}H_9N_2)(P(C_2H_5)_3)_2$

H	L	FOBS	FCAL
K = 0**			
-18	0	580	508
-14	0	1038	1056
-12	0	2639	2626
-10	0	2308	2316
-8	0	798	856
-6	0	712	635
-4	0	1670	1546
-2	0	5798	4944
0	2	4944	3639
2	2	3929	3313
-2	2	5653	5630
-14	2	909	972
-12	2	2414	2350
-10	2	3020	3231
-8	2	2221	2237
-6	2	780	729
-5	2	178	111
-4	2	784	895
4	2	4193	3985
6	2	2312	2595
8	2	725	808
10	2	1287	1291
12	2	870	876
14	2	840	865
16	2	1147	1156
18	2	388	264
-6	4	7160	6551
-4	4	8888	7521
2	4	2974	3113
-18	4	866	874
-16	4	760	677
-12	4	1170	1095
-10	4	1657	1776
-9	4	245	307
-8	4	2978	2860
-5	4	456	505
-3	4	506	572
-2	4	3682	2971
-1	4	302	365
0	4	775	756
1	4	226	82
3	4	251	237
4	4	3843	3793
5	4	187	266
6	4	3521	3426
8	4	953	983
10	4	348	348
12	4	476	508
14	4	1379	1427
16	4	425	459
-6	6	6320	6009
12	6	1032	1045
-8	6	4111	4347
-16	6	1092	1002
-14	6	306	326
-12	6	370	168
-10	6	948	1091
-7	6	326	259
-5	6	364	325
-4	6	225	330
-2	6	692	606
-1	6	173	286
0	6	1786	1647
1	6	392	413
2	6	2882	2732
4	6	2698	2717
5	6	378	454
6	6	2389	2451
7	6	457	516
8	6	309	223
10	6	581	578
-8	6	4111	4347
0	8	1370	1458
-18	8	812	917
-16	8	1129	1123
-14	8	725	734
-13	8	267	253
-12	8	1087	933
-10	8	2609	2550
-9	8	363	376
-8	8	1989	2424
-6	8	1126	1049
-4	8	2123	2291
-2	8	1812	1939
2	8	1333	1261
4	8	734	723
6	8	794	822
8	8	1575	1687
9	8	298	148
10	8	1205	1150
-18	10	509	524
-16	10	1150	1118
-14	10	1511	1627
-12	10	1706	1827
-10	10	912	867
-9	10	346	256
-8	10	577	549
-7	10	251	260
-6	10	1991	2014
-4	10	2858	2840
-2	10	2611	2567
-1	10	338	418
0	10	1275	1336
1	10	252	288
6	10	1422	1442
8	10	1345	1371
11	10	327	296
10	12	373	142
16	12	1153	1183
-14	12	1791	1815
-12	12	894	1096
-10	12	281	220
-8	12	390	456
-6	12	803	816
-4	12	1638	1703
-3	12	328	160
-2	12	1532	1498
0	12	886	957
2	12	458	394
4	12	870	876
5	12	290	83
6	12	518	439
-14	14	612	629
-12	14	911	893
-10	14	1399	1385
-6	14	287	410
-5	14	325	120
-4	14	294	338
2	14	1229	1314
6	14	492	414
-8	14	775	743
0	14	938	1023
-12	16	737	880
-10	16	998	1045
-8	16	767	828
-6	16	421	167
-2	16	298	347
0	16	829	862
3	16	476	262
K = 1**			
2	0	441	417
3	0	408	337
4	0	1329	1350
6	0	308	353
7	0	300	249
8	0	150	259
9	0	409	374
11	0	1207	1282
12	0	461	701
13	0	1015	1011
15	0	603	607
16	0	340	382
17	0	485	464
-18	1	436	387
-17	1	436	398
-16	1	623	539
-14	1	678	716
-12	1	778	779
-7	1	154	69
-6	1	580	568
-5	1	1357	1330
-4	1	483	426
-3	1	775	740
1	1	352	286
3	1	1563	1508
4	1	1089	1364
5	1	533	596
6	1	472	452
10	1	705	677
12	1	672	803
14	1	585	829
16	1	410	530
17	2	300	318
15	2	594	823
14	2	332	627
13	2	1035	1058
12	2	518	581
11	2	944	1007
10	2	563	574
9	2	931	999
7	2	223	330
6	2	273	261
5	2	513	499
3	2	1448	1375
2	2	1614	1469
1	2	382	328
0	2	167	160
-1	2	155	174
-2	2	178	177
-4	2	787	703
-5	2	1295	1217
-6	2	1332	1226
-7	2	758	765
-8	2	297	314
-9	2	705	801
-10	2	268	249
-11	2	715	751
-13	2	813	716
-14	2	282	260
-15	2	366	445
-17	2	386	301
-19	2	381	427
-18	3	479	361
-14	3	303	318
-10	3	483	551
-9	3	480	551
-8	3	610	597
-7	3	801	730
-6	3	696	608
-5	3	948	942
-3	3	418	355
-2	3	557	544
-1	3	303	412
0	3	167	75
1	3	1313	1256
2	3	998	963
4	3	286	181
6	3	849	874
7	3	267	195
8	3	972	1063
10	3	735	839
11	3	358	420
12	3	836	866
13	3	440	545
9	3	486	502
14	3	595	676
12	4	450	441
11	4	704	721
10	4	360	271
9	4	674	711
8	4	492	515
7	4	1291	1250
6	4	399	411
5	4	1325	1390
4	4	670	718
2	4	610	590
1	4	825	860
0	4	1200	1205
-1	4	459	413
-2	4	625	629
-3	4	583	489
-4	4	399	356
-5	4	1046	886
-6	4	755	764
-7	4	374	295
-8	4	734	732
-9	4	239	250
-10	4	541	545
-11	4	496	430
-15	4	266	296
-17	4	521	402
-18	4	288	152
-19	4	483	408
17	4	443	459
15	4	384	520
13	4	649	733
-18	5	316	290
-12	5	425	464
-11	5	372	304
-9	5	412	432
-8	5	424	421
-7	5	644	592
-6	5	248	269
-3	5	449	491
-1	5	1184	1073
0	5	308	464
2	5	326	259
4	5	920	906
6	5	1341	1282
7	5	716	680
8	5	984	892
9	5	337	332
11	5	438	412
12	5	486	453
14	5	334	241
16	5	353	385
15	6	526	543
11	6	304	280
10	6	491	431
9	6	816	796
8	6	451	402
7	6	1363	1357
6	6	1108	1155
5	6	1906	1945
4	6	804	752
3	6	1268	1218
1	6	352	360
0	6	475	464
-1	6	305	302
-2	6	497	476
-3	6	685	645
-6	6	228	145
-7	6	439	450
-8	6	567	634
-9	6	584	647
-12	6	361	276
-15	6	287	264
-17	6	348	378
-19	6	495	439
-11	6	655	720
-17	7	280	31
-14	7	317	268
-13	7	289	295
-6	7	235	211
-5	7	364	346
-4	7	270	369
-3	7	421	456
-2	7	327	360
2	7	1131	1196
3	7	546	600
4	7	1219	1274
5	7	784	785
6	7	1329	1365
7	7	589	659
8	7	1106	1052
9	7	270	370
10	7	414	383
14	7	421	327
15	7	407	371
-11	7	333	221
-10	7	307	274
-9	7	554	628
14	8	329	351
13	8	505	465
11	8	340	373
9	8	611	572
8	8	620	579
7	8	1326	1278
6	8	535	546
5	8	1306	1402
4	8	641	585
3	8	1196	1147
2	8	344	317
1	8	944	983
-2	8	249	261
-3	8	387	393
-4	8	723	800
-5	8	709	787
-7	8	319	366
-9	8	679	658
-10	8	449	392
-11	8	288	195
-15	8	336	263
-16	8	300	149
-17	8	330	258
-18	9	348	123
-16	9	337	220
-15	9	328	126
-7	9	401	381
-6	9	312	262
-5	9	519	547
-4	9	463	543
-2	9	448	443
0	9	929	983
2	9	727	710
3	9	476	496
4	9	778	787
6	9	273	317
8	9	907	930
7	9	455	471
8	9	786	743
11	9	377	354
12	9	534	514
13	9	399	428
10	9	401	397
12	10	453	432
11	10	822	874
10	10	417	422
9	10	744	719
7	10	562	518
6	10	578	593
5	10	684	647
3	10	758	762
2	10	450	448
1	10	842	913
0	10	786	666
-1	10	1135	1132
-2	10	515	455
-3	10	678	691
-4	10	255	67
-5	10	430	492
-6	10	350	338
-7	10	477	573
-12	10	390	391
-14	10	296	141
-14	11	350	200
-6	11	312	217
-4	11	776	781
-3	11	501	513
-2	11	1209	1245
0	11	956	952
1	11	528	538
2	11	767	749
4	11	450	374
6	11	484	503
5	11	455	549
10	11	679	754
11	11	466	503
10	12	577	507
9	12	903	865
8	12	441	418
7	12	629	667
6	12	288	96
4	12	335	376
3	12	543	416
1	12	949	968
0	12	343	406
-1	12	876	1187
-2	12	660	621
-3	12	1095	1069
-4	12	397	309
-5	12	576	532
-6	12	336	42
-8	12	313	155
-9	12	268	219
-11	12	308	296
-16	12	361	25
-11	13	297	217
-4	13	739	790
-3	13	458	468
-2	13	882	788
0	13	913	930
2	13	578	598
3	13	384	202
4	13	346	276
7	13	307	379
8	13	634	584
-6	13	321	314
-2	14	332	337
-3	14	718	731
-4	14	393	383
-5	14	614	566
-7	14	301	257
-9	14	275	201
-10	14	298	135
-12	14	278	290
7	14	638	569
5	14	548	529
3	14	365	270
2	14	457	426
1	14	634	581
0	14	351	391
-1	14	861	956
-14	15	293	64
-11	15	322	138
-10	15	408	365
-8	15	455	505
-6	15	378	441
-2	15	403	523
0	15	491	468
2	15	568	552
4	15	442	463
5	15	480	442
1	16	528	497
0	16	478	435
-1	16	427	377
-5	16	356	427
-7	16	340	427
-9	16	531	427
-3	16	384	459
-8	17	454	524
-6	17	326	363
K = 2**			
-1	0	6102	5404
-3	0	2198	2214
5	0	295	153
7	0	292	399
9	0	1371	1355
11	0	2365	2364
13	0	1481	1446
0	0	286	301
1	1	5110	4227
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TABLE I (*Continued*)

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1	2	485	430
4	3	500	473
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0	3	421	545
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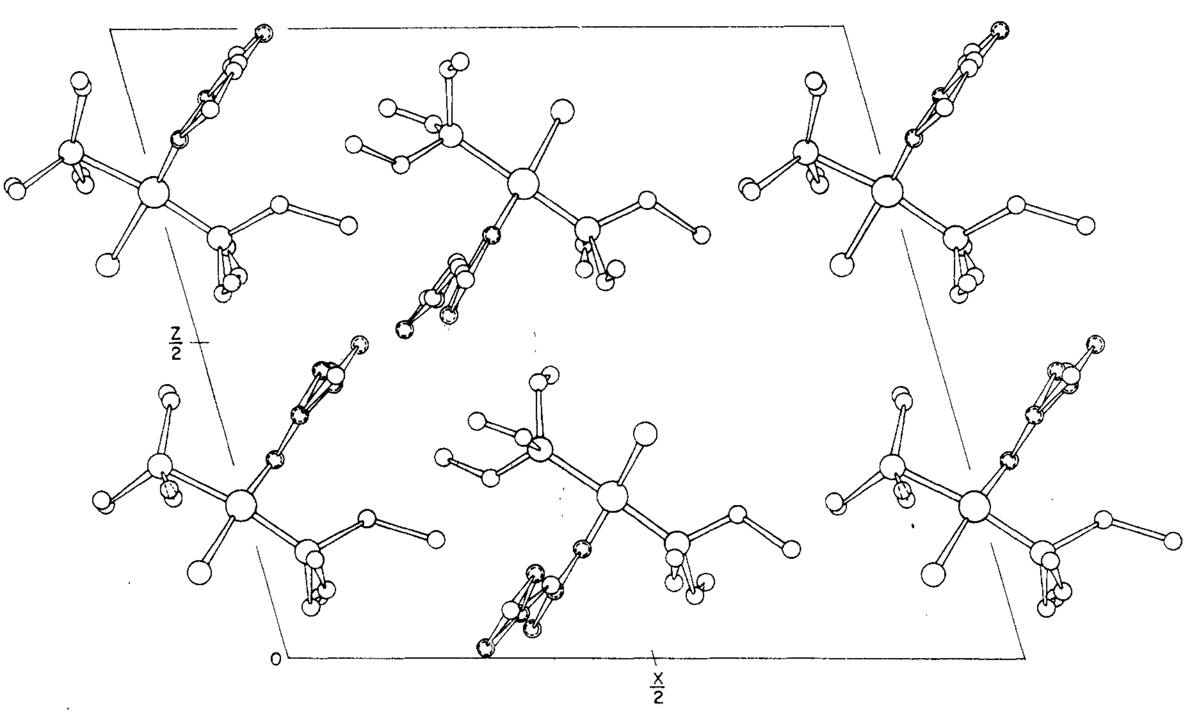

Figure 3.—Crystal packing of $PdCl(Azb)(P(C_2H_5)_3)_2$ viewed along the crystallographic *b* axis.

greater than 99.99%. Consequently, all final atom parameters are based on the ordered model which has a value of R_1 of 9.0%. This author does not, however, place confidence in the thermal parameters and bond distances involving these seven atoms (carbon–carbon distances range from 0.7 to 2.5 Å). Choosing the ordered model was shown to have virtually no effect on the parameters of the other atoms as they are essentially uncorrelated with those for the seven carbon atoms.

Scattering factors used for the neutral light atoms were those given by Ibers.[10] The values of the palladium atom scattering factors[11] were corrected for

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[10] J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

[11] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

TABLE II

Final Positional and Thermal Parameters[a]

Atom	x	y	z	B,[b] Å^2
Pd(1)[c]	0.5073 (1)	0.4417 (1)	0.2610 (1)	3.82
Pd(2)	0.9899 (1)	0.2038 (1)	0.2373 (1)	3.95
Cl(1)	0.5873 (3)	0.5091 (4)	0.3696 (4)	5.86
Cl(2)	0.9061 (4)	0.2664 (5)	0.1291 (4)	7.24
P(1)	0.5853 (5)	0.4532 (4)	0.1819 (5)	4.74
P(2)	0.4227 (5)	0.4406 (5)	0.3313 (5)	5.90
P(3)	0.0764 (5)	0.2102 (5)	0.1698 (5)	5.44
P(4)	0.9086 (5)	0.2027 (5)	0.3111 (5)	6.21
N(1)	0.3887 (11)	0.5059 (12)	0.1158 (11)	4.83 (49)
N(2)	0.6618 (10)	0.0367 (12)	0.4330 (11)	5.48 (51)
N(3)	0.1075 (10)	0.2639 (11)	0.3884 (10)	3.90 (44)
N(4)	0.1610 (9)	0.2954 (11)	0.4331 (10)	4.68 (43)
C(1)	0.4410 (12)	0.3824 (14)	0.1731 (12)	4.57 (55)
C(2)	0.3898 (11)	0.4216 (14)	0.1109 (12)	3.44 (48)
C(3)	0.3439 (11)	0.3776 (14)	0.0458 (12)	4.22 (52)
C(4)	0.3463 (13)	0.2971 (15)	0.0450 (14)	4.67 (62)
C(5)	0.3926 (15)	0.2577 (16)	0.1063 (15)	6.52 (70)
C(6)	0.4422 (13)	0.2983 (14)	0.1725 (13)	4.74 (63)
C(7)	0.6634 (12)	0.1244 (14)	0.4244 (13)	4.47 (54)
C(8)	0.6176 (13)	0.1671 (16)	0.3647 (14)	6.04 (63)
C(9)	0.6247 (13)	0.2518 (16)	0.3679 (14)	6.14 (65)
C(10)	0.6815 (15)	0.2881 (15)	0.4275 (16)	6.60 (70)
C(11)	0.7280 (13)	0.2557 (16)	−0.0176 (14)	6.02 (64)
C(12)	0.7212 (12)	0.1586 (16)	0.4823 (13)	5.72 (61)
C(13)	0.0598 (11)	0.1431 (13)	0.3229 (11)	3.46 (48)
C(14)	0.1091 (13)	0.1776 (16)	0.3885 (14)	5.21 (61)
C(15)	0.1572 (12)	0.1337 (14)	0.4464 (13)	4.82 (57)
C(16)	0.1540 (13)	0.0516 (13)	0.4382 (14)	4.28 (61)
C(17)	0.1070 (13)	0.0139 (14)	0.3775 (13)	4.50 (54)
C(18)	0.0615 (13)	0.0566 (13)	0.3197 (13)	4.26 (59)
C(19)	0.1602 (12)	0.3835 (14)	0.4352 (12)	4.07 (51)
C(20)	0.1077 (12)	0.4300 (15)	0.3841 (13)	4.85 (55)
C(21)	0.8846 (15)	0.0110 (18)	0.1089 (16)	7.10 (75)
C(22)	0.8270 (18)	0.0455 (17)	0.0499 (19)	8.50 (90)
C(23)	0.2248 (12)	0.5004 (15)	0.4991 (13)	5.36 (59)
C(24)	0.2179 (12)	0.4137 (15)	0.4911 (13)	5.76 (63)
C(1)$E(1)P(1)$[d]	0.4344 (16)	0.0447 (17)	0.3786 (17)	7.98 (86)
C(2)$E(1)P(1)$	0.4214 (17)	0.1210 (21)	0.3258 (18)	10.70 (99)
C(1)$E(2)P(1)$	0.5776 (14)	0.3843 (18)	0.0974 (16)	7.67 (74)
C(2)$E(2)P(2)$	0.6072 (19)	0.3026 (21)	0.1289 (20)	12.4 (11)
C(1)$E(3)P(1)$	0.6759 (13)	0.4587 (13)	0.2362 (13)	5.01 (59)
C(2)$E(3)P(1)$	0.7320 (17)	0.4762 (18)	0.1833 (18)	9.79 (92)
C(1)$E(1)P(2)$	0.5902 (19)	0.0644 (21)	0.1528 (20)	11.2 (11)
C(2)$E(1)P(2)$	0.6448 (27)	0.0592 (28)	0.1118 (30)	19.9 (19)
C(1)$E(2)P(2)$	0.3393 (21)	0.4061 (24)	0.2831 (22)	12.8 (12)
C(2)$E(2)P(2)$	0.2937 (30)	0.3820 (37)	0.3294 (32)	24.3 (24)
C(1)$E(3)P(2)$	0.4553 (18)	0.4083 (24)	0.4369 (20)	12.7 (11)
C(2)$E(3)P(2)$	0.4744 (16)	0.3207 (20)	0.4425 (17)	10.17 (94)
C(1)$E(1)P(3)$	0.0764 (16)	0.2975 (18)	0.1120 (17)	8.57 (88)
C(2)$E(1)P(3)$	0.0767 (16)	0.3741 (21)	0.1631 (18)	10.45 (98)
C(1)$E(2)P(3)$	0.0528 (20)	0.1396 (27)	0.0763 (22)	13.9 (13)
C(2)$E(2)P(3)$	0.0755 (18)	0.0693 (22)	0.1042 (21)	11.1 (10)
C(1)$E(3)P(3)$	0.1702 (15)	0.1986 (16)	0.2300 (16)	7.56 (78)
C(2)$E(3)P(3)$	0.2241 (15)	0.2083 (16)	0.1756 (16)	8.24 (77)
C(1)$E(1)P(4)$	0.9103 (47)	0.3455 (57)	0.3617 (51)	27.3 (41)
C(2)$E(1)P(4)$	0.9005 (50)	0.3483 (62)	0.3202 (52)	24.0 (47)
C(1)$E(2)P(4)$	0.8155 (31)	0.1392 (40)	0.2465 (33)	23.6 (25)
C(2)$E(2)P(4)$	0.8098 (46)	0.2225 (52)	0.2664 (45)	34.5 (36)
C(1)$E(3)P(4)$	0.9306 (19)	0.1814 (23)	0.4130 (21)	11.9 (11)
C(2)$E(3)P(4)$	0.9312 (20)	0.0946 (27)	0.4293 (21)	14.0 (13)

Anisotropic Temperature Parameters[e] (×10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd(1)	27.9 (10)	34.7 (9)	30.6 (9)	−2.1 (7)	5.3 (7)	−3.1 (7)
Pd(2)	27.6 (10)	38.0 (10)	30.8 (9)	−1.8 (8)	4.7 (7)	7.1 (8)
Cl(1)	32.5 (29)	73.0 (44)	39.7 (32)	−7.3 (28)	4.7 (24)	−16.0 (29)
Cl(2)	45.0 (33)	76.0 (48)	46.5 (34)	7.2 (31)	−9.9 (26)	21.0 (31)
P(1)	32.6 (38)	44.8 (42)	40.6 (38)	−3.7 (25)	9.5 (28)	0.9 (3)
P(2)	42.4 (43)	71.1 (55)	35.3 (38)	−5.9 (32)	13.3 (31)	1.7 (30)
P(3)	40.2 (41)	54.6 (48)	45.0 (40)	−8.3 (30)	18.6 (32)	0.0 (3)
P(4)	26.7 (35)	85.1 (61)	50.1 (42)	0.9 (3)	14.1 (30)	8.9 (4)

[a] Numbers in parentheses are esd's in the last figure quoted. [b] Equivalent isotropic B's are quoted here for the anisotropically refined atoms. [c] Pd(1) is the palladium atom in the first crystallographically independent molecule. [d] C(1)$E(1)P(1)$ is carbon atom 1 on ethyl group 1 bonded to phosphorus atom 1, etc. [e] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

the real ($\Delta f' = 1.13$ e$^-$) and imaginary ($\Delta f'' = 1.27$ e$^-$) components[12] of anomalous dispersion. Major computer programs used in the resolution of the structure were as follows: Patterson and Fourier synthesis, Zalkin's FORDAP; structure factor calculations and least-squares refinement, Prewitt's SFLS-5.

The final error of an observation of unit weight is 2.03. This probably reflects the unsatisfactory resolution of the disorder of the seven ethyl carbon atoms. The largest change of a positional or thermal parameter in the final structure factor calculation was 0.40σ and the average shift was 0.05σ. The highest peak of 0.93 e$^-$/Å^3 on a final difference electron density map, which has an estimated standard deviation[13] $\sigma(\Delta\rho) = 0.15$ e$^-$/Å^3, is in the vicinity of the Pd(2) atom. A final structure factor calculation for the 3452 unobserved data showed seven reflections for which $|F_c|$ was greater than twice the minimum observable. Table I lists the observed amplitudes, $10|F_o|$, and the final calculated structure factors, $10F_c$, each in electrons. The positional and thermal parameters derived from the final cycle of full-matrix least-squares refinement of the ordered model are given in Table II. The anisotropy of the thermal motion of the Pd, Cl, and P atoms is small. The direction of maximum vibration is that generally expected, *e.g.*, the major axis of the thermal ellipsoid for the chlorine atoms is perpendicular to the direction of the Pd–Cl bond and to the plane of the coordinating atoms.

Results and Discussion

The crystal structure is composed of discrete molecules of *trans*-PdCl(Azb)(P(C$_2$H$_5$)$_3$)$_2$, Azb = 2-(phenylazo)phenyl group, separated by normal van der Waals distances. There are two crystallographically independent, but essentially equivalent, molecules of the complex in the asymmetric portion of the unit cell. Use of statistical tests shows that there are no significant differences in the bond lengths (excluding distances within the triethylphosphine ligands) of these two crystallographically distinct molecules. The criterion[14] adopted for equivalence of bond lengths is that $t_0 = |l_1 - l_2|/(\sigma_1^2 + \sigma_2^2)^{1/2}$ must not exceed 3.0, where l_1 and l_2 are comparable bond lengths in molecule 1 and 2 and σ_1 and σ_2 are their respective standard deviations. The value of 3.0 is exceeded for a few of the bond angles, but this is probably due to intra- and intermolecular packing distortions of these angles. Table III gives selected interatomic bond distances and Table IV gives some bond angles for the molecules. Figures 1 and 2, show, respectively, a molecule of PdCl(Azb)(P(C$_2$H$_5$)$_3$)$_2$ and the inner coordination sphere around the Pd(1) atom including the 2-(phenylazo)phenyl group. A view of the crystal packing projected down the crystallographic b axis is shown in Figure 3.

The palladium atom is four-coordinate and is surrounded in an approximately planar fashion by two *trans* phosphorus atoms of the triethylphosphine lig-

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(12) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(13) H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons Ltd., London, 1953, p 308.

(14) D. W. J. Cruickshank and A. P. Robertson, *Acta Crystallogr.*, **6**, 698 (1953).

TABLE III

SELECTED INTERATOMIC DISTANCES,[a] Å

(a) Bond Lengths in the Inner Coordination Sphere

Bond	Pd(1)[b] distance	Bond	Pd(2) distance
Pd(1)–C(1)	1.983 (22)	Pd(2)–C(13)	2.004 (20)
Pd(1)–Cl(1)	2.386 (7)	Pd(2)–Cl(2)	2.379 (7)
Pd(1)–P(1)	2.323 (9)	Pd(2)–P(3)	2.306 (9)
Pd(1)–P(2)	2.307 (9)	Pd(2)–P(4)	2.299 (9)
		Wtd av[c] for 4 Pd–P bonds	2.306 (5)

(b) Bond Distances within the 2-(Phenylazo)phenyl Groups

Bond	Azb(1)[d]	Bond	Azb(2)
C(1)–C(2)	1.42 (3)	C(13)–C(14)	1.40 (3)
C(2)–C(3)	1.44 (3)	C(14–C(15)	1.39 (3)
C(3)–C(4)	1.34 (3)	C(15)–C(16)	1.38 (3)
C(4)–C(5)	1.37 (4)	C(16)–C(17)	1.35 (3)
C(5)–C(6)	1.46 (3)	C(17)–C(18)	1.35 (3)
C(6)–C(1)	1.40 (3)	C(18)–C(13)	1.45 (3)
C(7)–C(8)	1.37 (3)	C(19)–C(20)	1.37 (3)
C(8 –C(9)	1.42 (4)	C(20)–C(21)	1.46 (4)
C(9)–C(10)	1.43 (4)	C(21)–C(22)	1.36 (4)
C(10–(C(11)	1.34 (4)	C(22)–C(23)	1.42 (4)
C(11)–C(12)	1.44 (4)	C(23)–C(24)	1.36 (4)
C(12)–C(7)	1.42 (3)	C(24)–C(19)	1.40 (3)
Wtd av of 12 C–C bonds	1.406 (10)	Wtd av of 12 C–C bonds	1.389 (10)
		Wtd av for all 24 C–C bonds	1.397 (7)
N(1)–N(2)	1.23 (3)	N(3)–N(4)	1.24 (3)
C(2)–N(1)	1.41 (3)	C(14)–N(3)	1.44 (3)
C(7)–N(2)	1.47 (3)	C(19)–N(4)	1.47 (3)

(c) Bond Distances within the Triethylphosphine Ligands[e]

Phosphorus–Carbon

P(1)–C(1)*E(1)P(1)*[f]	1.84 (3)	P(3)–*C(1)E(1)P(3)*	1.77 (3)
P(1)–C(1)*E(2)P(1)*	1.84 (3)	P(3)–C(1)*E(2)P(3)*	1.96 (4)
P(1)–C(1)*E(3)P(1)*	1.77 (3)	P(3)–C(1)*E(3)P(3)*	1.86 (3)
P(2)–C(1)*E(2)P(2)*	1.72 (4)	P(4)–C(1)*E(3)P(4)*	1.75 (4)
P(2)–C(1)*E(3)P(2)*	1.86 (4)		
		Wtd av for 9 P–C bonds	1.82 (1)

Carbon–Carbon

C(1)*E(1)P(1)*–C(2)*E(1)P(1)*	1.55 (4)	C(1)*E(1)P(3)*–C(2)*E(1)P(3)*	1.56 (4)
C(1)*E(2)P(1)*–C(2)*E(2)P(1)*	1.52 (4)	C(1)*E(2)P(3)*–C(2)*E(2)P(3)*	1.30 (6)
C(1)*E(3)P(1)*–C(2)*E(3)P(1)*	1.64 (4)	C(1)*E(3)P(3)*–C(2)*E(3)P(3)*	1.60 (4)
C(1)*E(2)P(2)*–C(2)*E(2)P(2)*	1.41 (6)	C(1)*E(3)P(4)*–C(1)*E(3)P(4)*	1.48 (6)
C(1)*E(3)P(2)*–C(2)*E(3)P(2)*	1.51 (5)		
		Wtd av for 9 C–C bonds	1.53 (2)

(d) Selected Intramolecular Nonbonding Distances

Pd(1)–N(1)	3.12 (2)	Pd(2)–N(3)	3.15 (2)
Pd(1)–N(2)	4.34 (2)	Pd(2)–N(4)	4.35 (2)
P(1)–Cl(1)	3.39 (1)	P(3)–Cl(2)	3.34 (1)
P(2)–Cl(1)	3.30 (1)	P(4)–Cl(2)	3.33 (1)
P(1)–C(1)	3.02 (2)	P(3)–C(13)	2.99 (2)
P(2)–C(1)	3.04 (2)	P(4)–C(13)	3.07 (2)
Cl(1)–C(1)*E(3)P(1)*	3.36 (2)	Cl_2–C(1)*E(1)P(3)*	3.46 (3)
Cl(1)–C(1)*E(2)P(1)*	3.51 (3)	Cl(2)–C(2)*E(1)P(3)*	3.69 (3)
Cl(1)–C(1)*E(3)P(2)*	3.53 (3)	C(1)–C(1)*E(2)P(1)*	3.28 (3)
C(1)–C(1)*E(2)P(2)*	3.14 (4)	C(2)–C(1)*E(2)P(2)*	3.42 (4)
Pd(1)–C(2)	3.00 (2)	Pd(2)–C(14)	3.04 (2)
Pd(1)–C(6)	2.94 (2)	Pd(2)–C(18)	3.00 (2)
Pd(1)–Pd(2)	10.76 (3)		

[a] The numbers in parentheses are estimated standard deviations in the last significant figure listed. [b] Pd(1) is the palladium atom in the first crystallographically independent molecule. [c] Weighted average ($\bar{l}$) of bond lengths, l, are given by the formula $\bar{l} = \Sigma(l_i/\sigma_i^2)/\Sigma(1/\sigma_i^2)$, where σ_i is the estimated standard deviation derived from the least-squares refinement. The standard deviation of $\bar{l}$ is given by $\sigma(\bar{l}) = 1/[\Sigma(1/\sigma_i^2)]^{1/2}$. [d] Azb(1) = 2-(phenylazo)phenyl group bonded to atom Pd(1). [e] No bond lengths involving the seven disordered carbon atoms are listed. See text. [f] C(1)*E(1)P(1)* is carbon atom 1 on ethyl group 1 bonded to phosphorus atom 1, etc.

TABLE IV

SELECTED BOND ANGLES (DEGREES)

(a) Angles around the Palladium Atoms

Angle	Pd(1)	Angle	Pd(2)
P(1)–Pd(1)–Cl(1)	92.2 (3)	P(3)–Pd(2)–Cl(2)	91.0 (3)
Cl(1)–Pd(1)–P(2)	89.5 (3)	Cl(2)–Pd(2)–P(4)	90.9 (3)
P(2)–Pd(1)–C(1)	89.8 (7)	P(4)–Pd(2)–C(13)	90.7 (6)
C(1)–Pd(1)–P(1)	88.7 (6)	C(13)–Pd(2)–P(3)	87.6 (6)
Cl(1)–Pd(1)–C(1)	178.1 (7)	Cl(2)–Pd(2)–C(13)	175.3 (6)
P(1)–Pd(1)–P(2)	174.0 (3)	P(3)–Pd(2)–P(4)	176.1 (3)

(b) Angles within the 2-(Phenylazo)phenyl Groups

Angle	Azb(1)	Angle	Azb(2)
C(1)–C(2)–C(3)	121.7 (2.0)	C(13)–C(14)–C(15)	123.8 (2.3)
C(2)–C(3)–C(4)	120.1 (2.0)	C(14)–C(15)–C(16)	116.5 (2.0)
C(3)–C(4)–C(5)	119.3 (2.3)	C(15)–C(16)–C(17)	123.1 (2.1)
C(4)–C(5)–C(6)	123.5 (2.3)	C(16)–C(17)–C(18)	120.5 (2.2)
C(5)–C(6)–C(1)	117.5 (2.2)	C(17)–C(18)–C(13)	120.9 (2.1)
C(6)–C(1)–C(2)	117.7 (2.0)	C(18)–C(13)–C(14)	115.1 (2.0)
C(7)–C(8)–C(9)	116.8 (2.3)	C(19)–C(20)–C(21)	116.7 (2.1)
C(8)–C(9)–C(10)	119.8 (2.3)	C(20)–C(21)–C(22)	120.9 (2.3)
C(9)–C(10)–C(11)	121.8 (2.4)	C(21)–C(22)–C(23)	122.5 (2.3)
C(10)–C(11)–C(12)	119.8 (2.2)	C(22)–C(23)–C(24)	117.1 (2.3)
C(11)–C(12)–C(7)	117.3 (2.0)	C(23)–C(24)–C(19)	118.1 (2.0)
C(12)–C(7)–C(8)	124.1 (2.2)	C(24)–C(19)–C(20)	124.7 (2.2)
C(1)–C(2)–N(1)	115.6 (1.9)	C(13)–C(14)–N(3)	113.6 (2.0)
C(3)–C(2)–N(1)	122.7 (2.0)	C(15)–C(14)–N(3)	122.6 (2.1)
C(8)–C(7)–N(2)	124.5 (2.0)	C(20)–C(19)–N(4)	123.3 (1.9)
C(12)–C(7)–N(2)	111.3 (1.9)	C(24)–C(19)–N(4)	111.9 (1.8)
C(2)–N(1)–N(2)	113.5 (1.8)	C(14)–N(3)–N(4)	114.1 (1.9)
C(7)–N(2)–N(1)	112.4 (1.9)	C(19)–N(4)–N(3)	115.3 (1.7)
Pd(1)–C(1)–C(2)	122.6 (1.6)	Pd(2)–C(13)–C(14)	119.6 (1.5)
Pd(1)–C(1)–C(6)	119.7 (1.5)	Pd(2)–C(13)–C(18)	125.3 (1.7)
C(5)–C(2)–N(1)	178.2 (2.0)	C(17)–C(14)–N(3)	176.0 (2.0)
C(10)–C(7)–N(2)	170.0 (2.0)	C(22)–C(19)–N(4)	173.9 (2.0)

(c) Angles within the Triethylphosphine Ligand

Angle	Pd(1)	Angle	Pd(2)
	Pd–P–C Angles		
Pd(1)–P(1)–C(*1*)*E*(*1*)*P*(*1*)	109.9 (1.0)	Pd(2)–P(3)–C(1)*E*(*1*)*P*(*3*)	116.2 (1.0)
Pd(1)–P(1)–C(1)*E*(*2*)*P*(*1*)	119.9 (1.0)	Pd(2)–P(3)–C(1)*E*(*2*)*P*(*3*)	110.9 (1.3)
Pd(1)–P(1)–C(1)*E*(*3*)*P*(*1*)	114.1 (0.8)	Pd(2)–P(3)–C(1)*E*(*3*)*P*(*3*)	116.9 (0.9)
Pd(1)–P(2)–C(1)*E*(*2*)*P*(*2*)	117.6 (1.4)	Pd(2)–P(4)–C(1)*E*(*3*)*P*(*4*)	123.7 (1.6)
Pd(1)–P(2)–C(1)*E*(*3*)*P*(*2*)	115.2 (0.8)		
	C–P–C Angles		
C(1)*E*(*1*)*P*(*1*)–P–C(1)*E*(*2*)*P*(*1*)	95.7 (1.3)	C(1)*E*(*1*)*P*(*3*)–P(3)–C(1)*E*(*2*)*P*(*3*)	93.3 (1.7)
C(1)*E*(*1*)*P*(*1*)–P(1)–C(1)*E*(*3*)*P*(*1*)	106.7 (1.0)	C(1)*E*(*1*)*P*(*3*)–P(3)–C(1)*E*(*3*)*P*(*3*)	104.7 (1.4)
C(1)*E*(*2*)*P*(*1*)–P(1)–C(1)*E*(*1*)*P*(*1*)	108.3 (1.2)	C(1)*E*(*2*)*P*)*3*)–P(3)–C(1)*E*(*3*)*P*(*3*)	112.4 (1.6)
C(1)*E*(*2*)*P*(*2*)–P(2)–C(1)*E*(*3*)*P*(*2*)	114.4 (1.8)		
	P–C–C Angles		
P(1)–C(1)*E*(*1*)*P*(*1*)–C(2)*E*(*1*)*P*(*1*)	111.5 (2.0)	P(3)–C(1)*E*(*1*)*P*(*3*)–C(2)*E*(*1*)*P*(*3*)	110.5 (2.0)
P(1)–C(1)*E*(*2*)*P*(*1*)–C(2)*E*(*2*)*P*(*1*)	109.2 (2.0)	P(3)–C(1)*E*(*2*)*P*(*3*)–C(2)*E*(*2*)*P*(*3*)	104.5 (2.1)
P(1)–C(1)*E*(*3*)*P*(*1*)–C(2)*E*(*3*)*P*(*1*)	115.6 (1.7)	P(3)–C(1)*E*(*3*)*P*(*3*)–C(2)*E*(*3*)*P*(*3*)	111.0 (1.9)
P(2)–C(1)*E*(*2*)*P*(*2*)–C(2)*E*(*2*)*P*(*2*)	118.5 (2.0)	P(4)–C(1)*E*(*3*)*P*(*4*)–C(2)*E*(*3*)*P*(*4*)	112.5 (2.4)
P(2)–C(1)*E*(*3*)*P*(*2*)–C(2)*E*(*3*)*P*(*2*)	111.0 (2.0)		

ands, a chlorine atom, and a σ-bonded carbon atom of the 2-(phenylazo)phenyl group. The nitrogen atoms of the 2-(phenylazo)phenyl group are not bonded to the palladium atom, since the closest palladium–nitrogen distance is 3.12 Å. If a carbon–hydrogen bond distance of 1.10 Å is assumed, the closest approach of a phenyl-group hydrogen atom to either palladium atom is 3.00 Å.

An average value of 1.994 (15) Å was found for the two palladium–carbon distances. There appears to be no appreciable π interaction between these two atoms since a Pd–C(sp^2) distance of 2.05 Å would be expected from the sum of covalent radii. A Pt–γ-carbon bond distance[15] of 2.11 (2) Å was found in the complex K[Pt(acac)$_2$Cl].

Table V lists bond lengths for some four-coordinate palladium and platinum(II) complexes. As is seen in the table, the average Pd–Cl bond length of 2.382 (5) Å, determined for the present complex, is greater than that predicted from available covalent radii. (It is not, however, as long as the Pt–Cl bond *trans* to a hydrogen atom in[16] PtH(Cl)(P(C$_6$H$_5$)(C$_2$H$_5$)$_2$)$_2$.)

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[15] R. Mason, G. B. Robertson, and P. J. Pauling, *J. Chem. Soc. A*, 485 (1969).

[16] R. E. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

TABLE V

A COMPARISON OF BOND LENGTHS IN SOME SQUARE-PLANAR PALLADIUM AND PLATINUM COMPLEXES

Compound	Pd–P or Pt–P[a] distance, Å	*trans* ligand
cis-$PtCl_2(P(CH_3)_3)_2$[c]	2.247 (6)	Cl
trans-$PtH(Cl)(P(C_6H_5)_2(C_2H_5))_2$[d]	2.268 (6)	$P(C_6H_5)_2(C_2H_5)$
trans-$PtCl_2(P(C_2H_5)_3)_2$[e]	2.298 (18)	$P(C_2H_5)_3$
trans-$PdCl(Azb)(P(C_2H_5)_3)_2$[f]	2.306 (5)	$P(C_2H_5)_3$
trans-$PtBr_2(P(C_2H_5)_3)_2$[e]	2.315 (4)	$P(C_2H_5)_3$
trans-$PtI_2(P(CH_3)_2(C_6H_5))_2$[g]	2.334 (7)	$P(CH_3)_2(C_6H_5)$
trans-$PtCl(CO)(P(C_2H_5)_3)_2^+$[h]	2.34	$P(C_2H_5)_3$
	Pd–Cl or Pt–Cl[b] Distance, Å	
trans-$PtCl_2(P(C_2H_5)_3)_2$[e]	2.294 (9)	Cl
trans-$PtCl(CO)(P(C_2H_5)_3)_2^+$[h]	2.30	CO
trans-$PtCl_2(NH_3)_2$[i]	2.32 (1)	Cl
cis-$PtCl_2(NH_3)_2$[i]	2.33 (1)	NH_3
cis-$PtCl_2(P(CH_3)_3)_2$[c]	2.376 (6)	$P(CH_3)_3$
trans-$PdCl(Azb)(P(C_2H_5)_3)_2$[f]	2.382 (5)	Azb
trans-$PtH(Cl)(P(C_6H_5)_2(C_2H_5))_2$[d]	2.422 (9)	H

[a] The sum of the Pd(II) or Pt(II) and P single-bond covalent radii is 2.41 Å: L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960. [b] The sum of the Pd(II) or Pt(II) and Cl single-bond covalent radii is 2.30 Å. [c] G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, **6**, 725 (1967). [d] R. E. Eisenberg and J. A. Ibers, *ibid.*, **4**, 773 (1965). [e] H. G. Messmer and E. L. Amma, *ibid.*, **5**, 1775 (1966). [f] This work. Azb = 2-(phenylazo)phenyl group. [g] N. A. Bailey and R. Mason, *J. Chem. Soc. A*, 2594 (1968). [h] H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *J. Amer. Chem. Soc.*, **89**, 3360 (1967). [i] G. H. W. Milburn and M. R. Truter, *J. Chem. Soc. A*, 1609 (1966).

The long palladium–chlorine band can be attributed to the "structural" *trans* effect of a σ-bonded aryl group. Similarly, in K[Pt(acac)Cl] the Pt–O bond lengths[15] *cis* and *trans* to the Pt–γ-carbon bond differ by 0.104 (14) Å. This lengthening of metal–ligand bonds *trans* to a σ-bonded alkyl or aryl carbon atom has also been noted in several six-coordinate complexes such as trimethyl(salicylaldehydato)platinum(IV),[17] acetylacetonyl-2,2′-bipyridyltrimethylplatinum(IV),[18] $[Rh(C_2H_5)(NH_3)_5]Br_2$,[19] and $IrCl_2(C_{15}H_{13}O)((CH_3)_2SO)_2$.[20]

The strength of the metal–phosphorus interaction in *trans* square-planar complexes appears to be related to the π-bonding capacity of the *cis* ligands.[21] Less dπ–dπ interaction seems to occur between the metal and the phosphines when the *cis* groups are strong π-acceptor ligands. The data in Table V are consistent with this idea since the average value of 2.306 (5) Å observed for the Pd–P bond length in the present complex is essentially equal to that found[22] in *trans*-$PtX_2(P(C_2H_5)_3)_2$, X = Cl and Br. Moreover, all three of these complexes have shorter M–P bond distances than those determined[23] in *trans*-$PtCl(CO)(P(C_2H_5)_3)_2^+$ which contains a *cis* CO group.

The least-squares plane (Table VI) containing the Pd, two P, Cl, and σ-bonded carbon atoms indicates that this portion of the molecule is significantly nonplanar, nor are the four ligand atoms surrounding the palladium atom planar. Moreover, there are slight but significant deviations of angles between the palladium atom and its nearest neighbors from their idealized values of 90 or 180°. These facts suggest, as is verified by some of the short intramolecular nonbonded distances listed in Table III, that there is considerable steric crowding in the vicinity of the palladium atom.

The σ-bonded 2-(phenylazo)phenyl group assumes a *trans* configuration and has average bond lengths and angles which do not differ significantly from those in *trans*-azobenzene[24] and *trans-p*-azotoluene.[25] The carbon–carbon distances within the phenyl rings range from 1.34 to 1.46 Å, with the average value being 1.397 (7) Å. This compares favorably with the accepted value (1.392 Å) and with the average value of 1.380 (3) Å found[24] in *trans*-azobenzene. The average N–N bond length of 1.23 (2) Å is in accord with Pauling's value[26] for a nitrogen–nitrogen double dond. The C–N bond lengths range from 1.41 (3) to 1.47 (3) Å (in azobenzene C–N = 1.433 (3) Å) which compare favorably with the value of 1.472 Å accepted for a carbon–nitrogen single bond.

The angles between the C–N bond and the phenyl ring are distorted in a similar manner to that found in *trans*-azobenzene. The steric interactions between C(3) and N(2) and between C(8) and N(1) (with similar repulsions occurring in the other ligand) cause one set of C–C–N angles to average about 113° and the other to average about 123°. The least-squares planes and dihedral angles given in Table VI show the phenyl groups to be rotated out of the best plane defined by the C–N–N–C group. (The C–N–N–C group is virtually planar in both molecules and there is essentially no bending of the phenyl groups out of this plane.) The average C–C–C angle at the σ-bonded carbon atoms is 116.4 (1.5)°. Although this decrease is only 2.4σ from the expected value of 120°, it appears to be characteristic[27] of this angle for all comparable transition metal–aryl complexes.

The average bonding parameters for the phosphine ligands compare favorably with those found in similar structures and with predictions from covalent radii sums, even though some of the carbon atoms of the ethyl groups experience high thermal motion and/or disorder.

The complex *trans*-$PdCl(Azb)(P(C_2H_5)_3)_2$ is a member of a new class of stable σ-bonded transition metal–carbon bonds containing the 2-(phenylazo)phenyl group.[28] Others include those described by Heck[4] and

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(17) M. R. Truter and R. C. Watling, *J. Chem. Soc. A*, 1955 (1967).

(18) A. G. Swallow and M. R. Truter, *Proc. Roy. Soc., Ser. A*, **266**, 527 (1962).

(19) A. C. Skapski and P. G. H. Troughton, *Chem. Commun.*, 666 (1969).

(20) M. McPartlin and R. Mason, *ibid.*, 545 (1967).

(21) P. B. Hitchcock, M. McPartlin, and R. Mason, *ibid.*, 1369 (1969).

(22) G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **5**, 1775 (1966).

(23) H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *J. Amer. Chem. Soc.*, **89**, 3360 (1967).

(24) C. J. Brown, *Acta Crystallogr.*, **21**, 146 (1966).

(25) C. J. Brown, *ibid.*, **21**, 155 (1966).

(26) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(27) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 266 (1969).

(28) A recent report describes some palladium complexes of the 2-(phenylazoxy)phenyl ligand: A. L. Balach and D. Petridis, *Inorg. Chem.*, **8**, 2247 (1969).

Table VI

Weighted[a] Least-Squares Planes of the Form[b] $AX + BY + CZ = D$

Plane no.	Atoms	A	B	C	D
1	Pd(1), P(1), P(2), Cl(1), C(1)	0.2856	−0.8873	0.3621	−2.514
2	Pd(2), P(3), P(4), Cl(2), C(13)	0.2090	0.8948	0.3946	4.350
3	P(1), P(2), Cl(1), C(1)	0.2783	−0.8932	0.3531	−2.700
4	P(3), P(4), Cl(2), C(13)	0.2038	0.8999	0.3856	4.353
5	C(1), C(2), C(3), C(4), C(5), C(6)	−0.8567	−0.0366	0.5146	−5.391
6	C(7), C(8), C(9), C(10), C(11), C(12)	−0.7932	−0.0787	0.6039	−4.951
7	C(13), C(14), C(15), C(16), C(17), C(18)	−0.8464	−0.0400	0.5310	3.085
8	C(19), C(20), C(21), C(22), C(23), C(24)	−0.7407	−0.0088	0.6718	4.054
9	C(2), N(1), N(2), C(7)	−0.7595	−0.0825	0.6453	−4.776
10	C(14), N(3), N(4), C(19)	−0.6619	−0.0220	0.7493	4.620

Distances of Atoms from the Planes (Å)[c]

Plane no	
1	Pd(1), 0.034; P(1), −0.074; P(2), −0.089; Cl(1), −0.003; C(1), 0.013
2	Pd(2), −0.009; P(3), 0.058; P(4), 0.060; Cl(2), −0.026; C(13), −0.148
3	P(1), −0.037; P(2), −0.045; Cl(1), 0.007; C(1), 0.192; [Pd(1)], 0.075
4	P(3), 0.044; P(4), 0.044; Cl(2), −0.014; C(13), −0.186; [Pd(2)], −0.024
5	C(1), −0.002; C(2), 0.021; C(3), −0.009; C(4), −0.010; C(5), 0.016; C(6), 0.004; [N(1)], 0.051; [N(2)], 0.258
6	C(7), −0.031; C(8), 0.034; C(9), −0.013; C(10), −0.009; C(11), 0.006; C(12), 0.014; [N(1)], −0.124; [N(2)], −0.06
7	C(13), 0.000; C(14), −0.011; C(15), 0.013; C(16), −0.005; C(17), −0.006; C(18), 0.010; [N(3)], −0.023; [N(4)], −0.349
8	C(19), 0.005; C(20), −0.007; C(21), −0.002; C(22), 0.018; C(23), −0.017; C(24), 0.003; [N(3)], 0.093; [N(4)], −0.024
9	C(2), 0.014; N(1), −0.014; N(2), −0.012; C(7), 0.016
10	C(18), 0.007; N(3), −0.005; N(4), −0.005; C(19), 0.005

Dihedral Angles between Planes

Planes	Angle, deg	Planes	Angle, deg
5–6	6.71	7–8	10.4
5–9	9.67	7–10	16.4
6–9	3.00	8–10	5.45

[a] Atoms are weighted by the reciprocals of their variances. [b] The direction cosines were computed in an orthogonal coordinate system in which X, Y, and Z are parallel to a, b, and c^*, respectively. [c] Atoms not included in the least-squares plane calculation are in brackets.

Cope and Siekman[3] as well as complexes of the formulation $PdCl(Azb)(PR_3)$[29] obtained by treatment of $[PdCl(Azb)]_2$ with 2 equiv of phosphine. These latter complexes appear to contain the 2-(phenylazo)phenyl group acting as a bidentate ligand and further reaction with the phosphine cleaves the Pd–N bond to form *trans*-$PdCl(Azb)(PR_3)_2$.

Acknowledgment.—I gratefully acknowledge stimulating discussions with Professors R. W. Siekman and R. F. Stewart.

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[29] R. W. Siekman, Ph.D. Thesis, Massachusetts Institute of Technology, 1965.